

AccuPyc[®] III

GAS DISPLACEMENT PYCNOMETER SERIES



micromeritics[®]

CALCULATIONS

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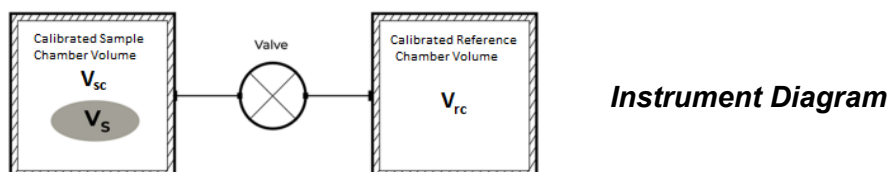
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ANALYSIS

GAS QUANTITY ACCOUNTING

A gas displacement pycnometer, such as the AccuPyc III, measures the volume of solid objects by a gas displacement method. The sample material may be of irregular, or regular shape, in powdered form or in one piece. A greatly simplified diagram of the instrument with sample material (denoted by V_s) is shown below:



During analysis, the temperature is held constant and the number of moles of gas is also held constant. Volumes are calculated by equating the amount of gas in the system before and after expansion from one chamber into the second chamber. The user may choose which chamber is filled initially, so either the sample chamber or the reference chamber may be the *fill* chamber. The analysis described below also takes into account the thermal expansion of the sample chamber and expansion chamber and also uses a real (non-ideal) gas equation of state in order to obtain the most precise measure of sample volume. The sample chamber may contain sample material or a reference ball. It can also have one or more inserts placed into it. It should be noted that the below analysis method is generally applicable to both the calibration procedure as well as sample volume measurement.

During an expansion cycle, three (absolute) pressures are measured:

- P_0 = The vent/atmospheric pressure in the expansion chamber before expansion.
- P_1 = The initial pressure after the fill in the fill chamber.
- P_2 = The final pressure in both the fill and expansion chamber.

Additionally, the following parameters are relevant to the analysis:

- T = The analysis temperature which is fixed during the measurements of P_0 , P_1 , and P_2 .
- $V_f(T)$ = The physical volume of the fill chamber at the analysis temperature T .
- $V_e(T)$ = The physical volume of the expansion chamber at the analysis temperature T .
- $Z_g(P, T)$ = The compressibility of the gas at pressure P and analysis Temperature T for gas g . The compressibility is part of the real equation of state which is:

$$Rn = \frac{PV}{Z_g(P, T)T}$$

where R is the ideal gas constant. Note the ideal gas constant will not appear in any of the results below because only the ratios of gas quantities will be used and R will factor out of these ratios.

After the *fill* chamber is charged with gas, and before the expansion, the quantity of gas in the chambers is expressed as follows:

$$Rn = \frac{V_f(T)P_1}{Z_g(P_1, T)T} + \frac{V_e(T)P_0}{Z_g(P_0, T)T}$$

then after expansion, the quantity of gas in the chambers is expressed as:

$$Rn = \frac{[V_f(T) + V_e(T)]P_2}{Z_g(P_2, T)T}$$

Since it is assumed no gas is lost, these two expressions are equal from which one obtains after some rearrangement, the expression:

$$\frac{V_f(T)}{V_e(T)} = \frac{\frac{P_2}{Z_g(P_2, T)} - \frac{P_0}{Z_g(P_0, T)}}{\frac{P_1}{Z_g(P_1, T)} - \frac{P_2}{Z_g(P_2, T)}} \equiv r(g, P_0, P_1, P_2, T)$$

The right-hand-side of the above equation is a function of the measured quantities, and it is convenient to define it as a function $r(g, P_0, P_1, P_2, T)$ referred to in the following as the ratio function. It should be noted that in the above expression, the volume terms $V_f T$, and $V_e T$ also account for the volume of the sample, reference ball or insert as part of their definition. The above expression is generally applicable and will be used for volume calibration and sample volume measurement next.

THERMAL EXPANSION

The volume of any solid changes as the solid expands or contracts with temperature changes. The formula for this is:

$$V(T) = V_0(1 + 3\alpha(T - T_0))$$

where V_0 is a volume measured at a specific temperature T_0 . α is the linear expansion coefficient. There will be a separate thermal expansion equation for each material used in the analysis. In particular, a single thermal expansion coefficient α_c will be known for the sample and reference chamber. The calibration procedure explained next will instead determine the V_0 parameters for the sample chamber and reference chamber.

CALIBRATION

Determination of the sample and reference chamber volumes by the below calibration method relies on a calibrated reference ball which has a thermal expansion equation with known constants. The sample chamber volume V_{sc} and reference chamber volume V_{rc} may be obtained by performing two analyses. The first analysis is an empty sample chamber analysis in which the sample chamber is filled with gas and then expanded to the reference chamber. The ratio function r defined previously is utilized to relate these volumes to measured quantities. In particular, the sample chamber is the *fill* chamber and the reference chamber is the *expansion* chamber from which one obtains:

$$\frac{V_{sc}(T)}{V_{rc}(T)} = r(g, P_0, P_1, P_2, T) = r_{sc}$$

where the ratio is written in shorthand as r_{sc} . The second analysis is the same as the first but with the ball in the sample chamber. This yields a second equation:

$$\frac{V_{sc}(T) - V_b(T)}{V_{rc}(T)} = r_{scb}$$

where the ratio r_{scb} has been introduced and where the volume of the reference ball $V_b(T)$ and its thermal expansion properties are also known. The previous two expressions may be combined to determine $V_{sc}(T)$ and $V_{rc}(T)$ both of which can be represented by the linear thermal expansion equation with the same thermal expansion coefficient α_c since the chambers are of the same material.

A separate calibration is done when the reference chamber is filled initially and the gas is expanded into the sample chamber. The sample chamber volume and reference chamber volume for this situation will be different than the preceding case due to an inlet volume being incorporated to the reference chamber instead of the sample chamber so the geometry of the chambers will have changed slightly. As a result, this case will result in different calibration parameter values compared to the above case, though the notation used will be the same for simplicity.

With the sample chamber empty, and the reference chamber being the *fill* chamber one obtains the ratio expression:

$$\frac{V_{rc}(T)}{V_{sc}(T)} = r_{rc}$$

where again, the ratio r_{rc} is the ratio function of measured quantities defined above. For the second analysis of this calibration the reference ball is placed in the sample chamber and again the ratio is obtained:

$$\frac{V_{rc}(T)}{V_{sc}(T) - V_b(T)} = r_{rcb}$$

Combining these last two expressions, the thermal expansion functions $V_{sc}(T)$ and $V_{rc}(T)$ may be obtained.

DETERMINATION OF SAMPLE VOLUME

A sample analysis to determine sample volume uses the calibrated sample chamber volume $V_{sc}(T)$ and calibrated reference chamber volume $V_{rc}(T)$ explained in the above. Additionally, the sample chamber may include a sample cup or other sample inserts whose thermal expansion properties are also previously calibrated and thus known.

To determine the sample volume, a sample material is placed into the sample chamber along with a possible calibrated insert. The sample chamber is filled, and expanded into the reference chamber. The ratio function is again applied with the *fill* chamber volume being the sample chamber (minus the sample and any inserts):

$$\frac{V_{sc}(T) - V_s - V_i(T)}{V_{rc}(T)} = r_{scsi}$$

where the sample volume is denoted V_s and the insert volume is $V_i(T)$. The sample volume can be solved trivially from this last expression:

$$V_s = V_{sc}(T) - V_i(T) - r_{scsi} V_{rc}$$

where all the quantities on the right-hand-side have been previously obtained by calibration or measured by the experiment.

Analysis using the reference chamber as the fill chamber can also be performed using the corresponding calibration volumes. In this case, one obtains:

$$\frac{V_{rc}(T)}{V_{sc}(T) - V_s - V_i(T)} = r_{rcsi}$$

and solving this equation for the sample volume:

$$V_s = V_{sc}(T) - V_i(T) - \left(\frac{1}{r_{rcsi}} \right) V_{rc}$$

RUN PRECISION

Run precision allows early termination of analysis once five consecutive runs achieve a user specified tolerance. The user specifies the tolerance as a fraction of the nominal sample chamber volume. Run precision is achieved when the following condition is met:

$$|V_s[i] - V_s[4]| \leq f_{tol} \cdot V_{nominal} \quad \text{for } i \in [0, 3]$$

where $V_s[0], V_s[1], V_s[2], \dots$ are the sample volumes measured in each of the five runs, with $V_s[4]$ being the most recent, $V_{nominal}$ is the sample chamber volume which would be 1, 10, 100, 350 and/or 2000 cm^3 . The fraction f_{tol} is entered by the user in the AccuPyc III application as a percentage of full scale.

SPECIFIC GRAVITY

The specific gravity is:

$$SG = \frac{\rho_s}{\rho_{H_2O}}$$

where ρ_s is the measured sample density and ρ_{H_2O} is the density of water at the analysis temperature.

TOTAL PORE VOLUME

The total pore volume per gram of sample is obtained from the entered envelope density as follows:

$$\begin{aligned}
 v_{pore} &= \frac{V_{envelope} - V_s}{m_s} \\
 &= \left(\frac{1}{\rho_{envelope}} - \frac{1}{\rho_s} \right) \\
 &= \frac{\rho_s - \rho_{envelope}}{\rho_s \cdot \rho_{envelope}}
 \end{aligned}$$

where m_s and ρ_s are sample mass and density, and where the measured sample volume V_s is the skeletal volume. If instead, the entered bulk density is used for the calculation, then the interstitial volume (volume between grains) is included on the left-hand-side:

$$\begin{aligned}
 v_{pore} + v_{interstitial} &= \frac{V_{bulk} - V_s}{m_s} \\
 &= \frac{\rho_s - \rho_{bulk}}{\rho_s \cdot \rho_{bulk}}
 \end{aligned}$$

If a single grain of sample material is being tested, then the interstitial volume is zero and the bulk volume is identical to the envelope volume.

PERCENT POROSITY

The percent porosity is obtained from the entered envelope density and the measured sample density which is approximately the skeletal density:

$$\mathcal{P}_{por} = \left(1 - \frac{\rho_{envelope}}{\rho_s} \right) \times 100\% \quad (1)$$

TOTAL SOLIDS CONCENTRATION

The total solids concentration is the percent of weight contributed by solids which is:

$$\mathcal{P}_{conc} = \left(1 - \frac{\rho_{liq}}{\rho_s}\right) \frac{\rho_{sol}}{\rho_{sol} - \rho_{liq}} \times 100\%$$

where ρ_{liq} is the entered liquid density, ρ_{sol} is the entered solid density, and ρ_s is the measured sample density.

ASPHALT DENSITY

Assuming the sample material is Asphalt measured at temperature T , one can convert this measured volume to the materials expected volume at 60° F from the below formula:

$$\begin{aligned}V_{60} &= V(T) \cdot a(T) \\a(T) &= AT^2 + BT + C \\A &= 4.498813 \times 10^{-8} \text{ }^\circ\text{F}^{-2} \\B &= -3.548988118 \times 10^4 \text{ }^\circ\text{F}^{-1} \\C &= 1.0211326242\end{aligned}$$

where T is the temperature in degrees F, $V(T)$ is the measured sample volume, and $a(T)$ is the thermal expansion factor for Asphalt. The density and specific gravity of asphalt at 60° F are then obtained:

$$\begin{aligned}\rho_{60} &= m_s / V_{60} \\SG_{60} &= \rho_{60} / \rho_{H_2O} \\ \rho_{H_2O} &= 0.9990170 \text{ g/ml}\end{aligned}$$

where ρ_{H_2O} is the density of water at 60° F.

FOAMPYC METHODS

GEOMETRIC VOLUME AND ACTIVE SURFACE AREA

Geometric volume V_{geom} of the sample is calculated based on the sample shape. In the below, N is the number of sample pieces, and the geometry of the pieces is either cubic, cylindrical or a rectangular prism:

$$V_{cube} = x^3 N$$

$$V_{cyl} = \pi \frac{hd^2}{4} N$$

$$V_{rect} = (xyz) N$$

The active area A_{geom} is the total geometric surface area of the sample excluding any sides which are covered by a *skin*. A skin is a thin film of plastic which seals the surface of the sample. The active area is needed for the FoamPyc corrections using the cell dimensions. Active surface area is obtained as follows:

$$A_{cube} = x^2(6 - M)N$$

$$A_{cyl} = (\pi dh + 2\pi d(2 - M)) N$$

$$A_{rect} = (xz(2 - M_x) + yz(2 - M_y) + xy(2 - M_z)) N$$

where in the case of cylindrical geometry, d and h are the cylinder diameter and height. In the case of cubic or rectangular prism geometries, x is the long edge, y is the short edge, and z is the other edge. The parameter M is the number of faces on the sample containing a *skin*.

RESIN VOLUME

The resin density is entered by the user when setting up FoamPyc analysis conditions. The resin volume is the sample mass divided by the user entered resin density:

$$V_r = \frac{m_s}{\rho_r}$$

The percent of volume contributed by the resin is then:

$$\mathcal{P}_r = \frac{V_r}{V_{geom}} \times 100\%$$

where V_{geom} is the geometric volume described in the previous section.

CALCULATED OPEN CELL FRACTION (CORRECTION USING CELL DIMENSIONS)

This method corrects for the cells damaged while cutting the sample to the necessary size and shape. This is accomplished by using either the average cell diameter or the cell chord length (as defined in ASTM method D-6226-15) and the measurements of the sample to determine the volume of the cut cells. The volume of cut cells is deducted from the total volume of the open cells measured by the pycnometer to obtain the volume of open cells which is the quantity of interest. Specifically, the percentage of open cells is:

$$\mathcal{P}_{open} = \frac{V_{geom} - V_s - V_{cut}}{V_{geom}} \times 100\%$$

$$V_{cut} \begin{cases} A \frac{x}{1.14}, & x = \text{chord length} \\ A \frac{x}{1.4515} & x = \text{cell diameter} \end{cases}$$

where V_s and V_{geom} are the measured and geometric volume of the sample, A is the active area, V_{cut} is the volume of cells cut open, and x is the chord length or cell diameter. The percentage of the resin plus closed cell volume is then:

$$\mathcal{P}_{resin+closed} = 100\% - \mathcal{P}_{open}$$

MEASURED OPEN CELL FRACTION (CORRECTION BY RECUTTING SAMPLE)

This method corrects for the cut cells by using two separate measurements. For the 2nd measurement, the sample is recut to double the amount of cut surface. The observed difference in cut open cell volume is applied as a correction to the initial measured volume. This method offers the distinct advantage of fewer assumptions made about the cell geometry.

$$V_{cut} = V_s[1] - V_s[2]$$

$$V_{resin+closed} = V_s[1] + V_{cut}$$

$$V_{open} = V_{geom} - V_{resin+closed}$$

$$\mathcal{P}_{closed} = \frac{V_{closed}}{V_{geom}} \times 100\%$$

$$\mathcal{P}_{open} = \frac{V_{open}}{V_{geom}} \times 100\%$$

where $V_s[1]$ is the sample volume from the first analysis (before cutting), and $V_s[2]$ is the sample volume from the second analysis (after cutting).

UNCORRECTED OPEN CELL FRACTION

This method does not correct for cut cells. It is used for materials with predominantly open cells where good accuracy can be achieved without correction. The accuracy level deteriorates as the percentage of closed cells increases.

$$V_{open} = V_{geom} - V_s$$

$$P_{open} = \frac{V_{open}}{V_{geom}} \times 100\%$$

COMPRESSIBILITY TEST

In this analysis method, the fill pressure is increased incrementally over the sample with each repeat of the P_1, P_2 cycle (where P_1 is the initial pressure to which the sample is charged, and P_2 the final pressure after expansion). The apparent variation of the measured sample volume with the average pressure is determined. This test is an approximate indication. It is not intended to be an exact measure of the volume compressibility.

Quantities appended with $[i]$ are for cycle $i \in [1, N]$, where N is the number of cycles.

$$\Delta V_1[i] = \frac{V_s[i-1] - V_s[i]}{P_1[i-1] - P_1[i]}$$

$$\Delta V_2[i] = \frac{V_s[i-1] - V_s[i]}{P_2[i-1] - P_2[i]}$$

$$P_1 = \frac{\left(\frac{1}{N} \sum_{i=1}^N \Delta V_1[i]\right)}{V_{geom}} \times 100\%$$

$$P_2 = \frac{\left(\frac{1}{N} \sum_{i=1}^N \Delta V_2[i]\right)}{V_{geom}} \times 100\%$$

where P_1, P_2 are the percentage of average change in volume over the set of cycles.

CELL FRACTURE TEST

In this analysis method, a perfectly rigid foam is assumed. First, a P_1, P_2 cycle is performed at the lower of two specified P_1 pressures, and the results stored. A second cycle is performed at a higher specified value of P_1 , then a third cycle identical to the first cycle is performed. The difference between the volume of the sample on the first measurement and on the third measurement is reported as the volume of fractured cells. It is assumed that cells fracture by exposure to the highest pressure (2nd cycle) so that when the third measurement is made, the measured sample volume has decreased from the first cycle by the amount of the closed cell volume which was fractured. The volume of fractured cells and the percent of fractured cells are obtained as follows:

$$\Delta V_{frac} = V_s[3] - V_s[1]$$
$$\mathcal{P}_{frac} = \frac{\Delta V_{frac}}{V_{geom}} \times 100\%$$

where $V_s[1]$ is the first measured sample volume for the pre-fracture cycle, $V_s[3]$ is the third measured sample volume for the post-fracture cycle.

SPC REPORT VARIABLES

REGRESSION CHART VARIABLES

The line of best fit for the *Regression Chart* is calculated by the usual least squares method.¹⁾ If there is only a single point or all N points have the same x -value, there can be no line of best fit in the standard form.

$$\bar{x} = \frac{1}{N} \sum_{i=1}^N x_i$$

$$\bar{y} = \frac{1}{N} \sum_{i=1}^N y_i$$

$$m = \frac{\sum_{i=1}^N (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^N (x_i - \bar{x})^2}$$

$$b = \bar{y} - m\bar{x}$$

where \bar{x} and \bar{y} denote the average values and m and b are the slope and y -intercept. The covariance and coefficient of correlation for this line is also calculated in the usual way.²⁾

$$\sigma_x = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N}}$$

$$\sigma_y = \sqrt{\frac{\sum (y_i - \bar{y})^2}{N}}$$

$$\text{Cov}(x, y) = \frac{1}{N} \sum (x_i - \bar{x})(y_i - \bar{y})$$

$$\text{Corr} = \frac{\text{Cov}(x, y)}{\sigma_x \sigma_y}$$

1) BASIC Scientific Subroutines Vol II, by F.R. Ruckdeschel, Copyright 1981 BYTE Publications/McGraw Hill, p. 16.

2) Mathematical Handbook for Scientists and Engineers, G.A. Korn and T.M. Korn, McGraw Hill, Sec. 18.4. (1968) |

CONTROL CHART VARIABLES

$$\bar{y} = \frac{1}{N} \sum y_i$$

$$\sigma_y = \sqrt{\frac{\sum (y_i - \mu)^2}{N - 1}}$$

$$\text{CoefVar} = \frac{\sigma_y}{\bar{y}}$$