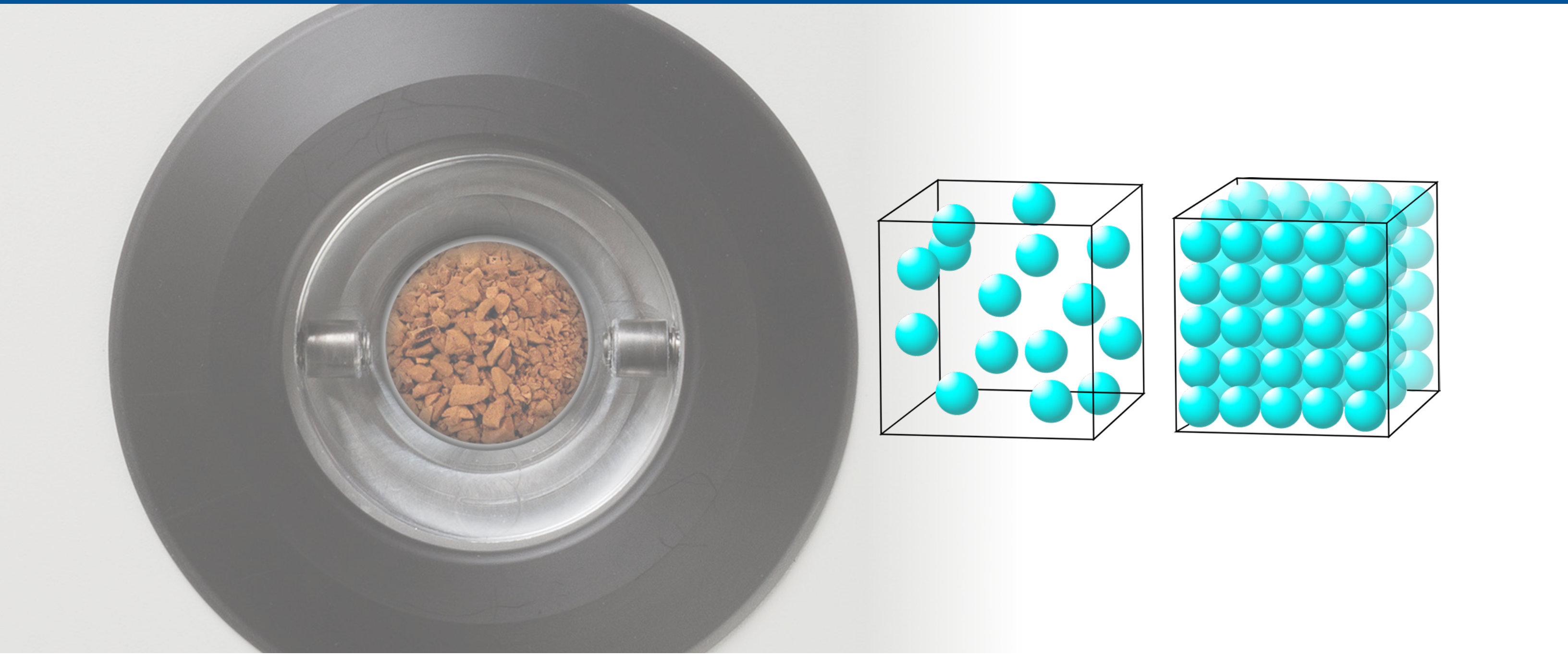
CAN I CALCULATE DENSITY FROM FREE SPACE?



A frequent question is often posed by users, can density be calculated from free space measured on a gas adsorption analyzer instead of using an instrument that is designed to obtain density? This tech note will explore the possibility of using such a method and compare with results obtained by the Micromeritics AccuPyc II.

Gas adsorption instruments measure quantity of gas adsorbed at various pressures. This information is used to calculate surface area and porosity information. To determine the quantity of gas that adsorbs on a sample, the system must determine the available volume within a sample tube not being occupied by the sample. The typical gas adsorption instrument establishes this free volume (also referred to as free space) by taking two measurements using helium, a non-adsorbing gas. The ambient free space is measured under ambient temperature while the analysis free space is measured at the analysis temperature.

The sample volume can be estimated by subtracting the ambient free space of an empty tube from the ambient free space of the same tube with sample. The density can then be calculated by dividing the sample's mass by the volume.

A helium pycnometer operates in a similar manner. The pycnometer is calibrated using a known volume, typically a sphere or a non-porous ceramic with well-defined geometry, known composition, and well-known coefficient of thermal expansion. A pycnometer calibration is used to establish the volumes of the reference and volume chambers. The sample is then placed in the sample chamber, and a process that is similar to free space determinations is employed to determine volume of the sample chamber that is occluded by the sample material. This process is repeated for typically 10 cycles to determine an average volume of the material under test.

Methods

In this case study, the ambient free space was obtained for empty 3/8 and 1/2-inch sample tubes. Analyses were performed on alumina, carbon black, stainless steel, tungsten, and tungsten carbide to determine the ambient free space. Samples were degassed properly to ensure cleanliness and weighed. Table 1 shows the ambient free space values, sample mass, and calculated volumes and densities.

The AccuPyc II calculates a sample's volume using Boyle's law. Temperature of the reference and sample chamber is not needed because both chambers are at the same temperature, within the same aluminum block. The sample chamber is pressurized above ambient pressure, pushing the analysis gas into pores to obtain an accurate volume of the material. Multiple cycles are performed to obtain an average sample volume.

Samples were removed from the gas adsorption sample tubes, then placed in the AccuPyc and analyzed at 20 °C to determine the skeletal density. The cell volume and expansion volumes were 5.7898 cm^3 and 8.3778 cm^3, respectively. Table 2 compares the density values obtained by the AccuPyc to the calculated values obtained through the free space subtraction method.

Results

Figure 1. Calculated and measured density versus expected density

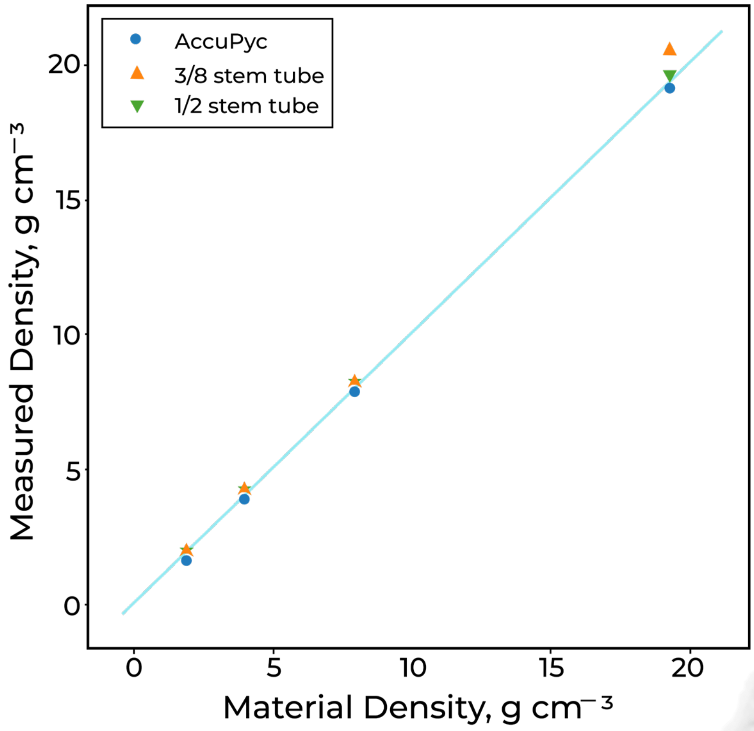


Table 1. Different materials used with their respective density values calculated from free space determinations

Sample	Sample Tube Diameter (in)	Sample Mass (g)	Free Space - Empty (cm³)	Free Space - Sample (cm³)	Volume Displaced (cm³)	Calculated Density (g/cm³)
Alumina	3/8	2.0333	10.1624	9.6885	0.4739	4.2906
Alumina	1/2	2.0025	15.0875	14.6123	0.4752	4.2140
Carbon Black	3/8	0.8231	9.0953	8.6962	0.3991	2.0624
Carbon Black	1/2	1.5965	15.8223	14.9907	0.8316	1.9198
Stainless Steel	3/8	7.3422	10.1624	9.2774	0.8850	8.2963
Stainless Steel	1/2	11.3741	15.0875	13.6854	1.4021	8.1122
Tungsten	3/8	15.6931	9.0953	8.3318	0.7635	20.5542
Tungsten	1/2	18.7127	15.8223	14.8641	0.9582	19.5290
Tungsten Carbide	3/8	9.6839	9.0953	8.5079	0.5874	16.4860
Tungsten Carbide	1/2	13.0748	15.1939	14.3654	0.8285	15.7813

Table 2. Summary of density values determined by Micromeritics AccuPyc II vs. free space subtraction method

Sample	Calculated Density 3/8" (g/cm³)	Calculated Density 1/2" (g/cm³)	AccuPyc Density (g/cm³)	Expected Density (g/cm³)	Sample Volume to Cell Volume
Alumina[1]	4.2906	4.2140	3.9590	3.95	0.1310
Carbon Black[2]	2.0624	1.9198	1.8907	1.90	0.1270
Stainless Steel	8.2963	8.1122	7.8592	7.93	0.2507
Tungsten	20.5542	19.5290	19.1721	19.28	0.1881
Tungsten Carbide	16.4860	15.7813	15.6422	15.63	0.1834

Table 3. Ratio of sample to free space volume

Sample	Sample Tube Diameter (in)	Sample Volume (cm³)	Free Space Volume (cm³)	Sample Volume to Free Space Volume
Alumina	3/8	0.4739	10.1624	0.0466
Alumina	1/2	0.4752	15.0875	0.0315
Carbon Black	3/8	0.3991	9.0953	0.0439
Carbon Black	1/2	0.8316	15.8223	0.0526
Stainless Steel	3/8	0.8850	10.1624	0.0871
Stainless Steel	1/2	1.4021	15.0875	0.0929
Tungsten	3/8	0.7635	9.0953	0.0839
Tungsten	1/2	0.9582	15.8223	0.0606
Tungsten Carbide	3/8	0.5874	9.0953	0.0646
Tungsten Carbide	1/2	0.8285	15.1939	0.0545

Summary

Densities measured on the AccuPyc were very close to expected values. Values obtained from the free space subtraction method were noticeably higher, Figure 1.

Using the ambient free space to determine density is an unconventional approach as it is generally not intended to be used for this purpose. The ambient free space measurement on the gas adsorption analyzer is conducted below atmospheric pressure and only performed once. The AccuPyc pressurizes the sample chamber above atmospheric pressure, ensuring gas enters pores open to the surface, and repeats this process multiple times. Ambient free space, both blank and sample, measured by gas adsorption will fluctuate depending on temperature, so both the empty tube free space and the free space with sample present should be obtained at the same ambient temperature to minimize errors. AccuPyc measurements are recorded in an isothermal environment. The AccuPyc utilizes high thermal conductivity materials of construction, and this design principle provides the stable temperature environment required for accurate displacement volume measurements.

The AccuPyc is optimized when the sample occupies the majority of the available volume within the sample chamber. A sample tube on a gas adsorption instrument would need to be filled to be equivalent, which is neither practical nor recommended. The sample volume to free space volume ratios can be seen in Table 3. These values are much lower than the sample volume to cell volume ratio obtained on the AccuPyc, displayed in Table 2.

The AccuPyc is designed to obtain accurate density results and is preferred over the subtraction method obtained from gas adsorption instruments, which are not optimized for density determination.

Reference Calculations

Ambient free space is determined by the following equation:

$$V_{ambFS} = \left(\frac{P_1}{P_2} V_{man} - V_{man}\right) \frac{T_{STD}}{T_{man}},$$

Where P_1 is the manifold pressure before dosing into sample tube, P_2 is manifold pressure after dosing into sample tube, V_{man} is manifold volume, T_{STD} is the standard temperature (273.15 K), and T_{man} is the manifold temperature.

Boyle's law

$$P_1V_1 = P_2V_2$$

References

1. Micromeritics Alumina Reference Material, Lot SA5214-19001A
2. Micromeritics Carbon Black Reference Material, Lot D-4

Micromeritics Instrument Corp.
4356 Communications Drive
Norcross, GA 30093

Tel.: +1 770 662-3636

info@micromeritics.com
micromeritics.com