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Measurement of specific surface area of powders using new method and instrumentation

By Jan Malczyk

Absolute method of determination of specific surface area of powders is being proposed. Development of a versatile volumetric analyzer, pV/T Master, and ancillary hardware allows for carrying out all measurements using one instrument. Better implementation of the permeametry technique can make it more effective in characterization of powders.

There have been many equations for determination of specific area of powders by measuring flow of gas through a packed bed of powder. The derivations are based on the Darcy law which states that the average fluid velocity is proportional to the pressure difference between the top and bottom of the bed and inversely proportional to the thickness of the bed. This law was obtained using incompressible fluids (water), but somehow it was applied to compressible gases flowing through a packed bed. More detailed experimental work had showed more complex then linear dependence of flow rate vs pressure differential and equations with higher then linear term were proposed. Our own work on measuring flow rates of air through packed beds of cement showed quadratic relationship and it was discussed in application note "*Proposal of quadratic equation for prediction of flow rates versus pressure in packed bed of cement*". Further theoretical concept was presented in another application note "*Absolute method for determination of specific surface area using gas (air) permeability technique*". Below is summary of this method needed for further discussion.

Let $\mathbf{S_a}$ [cm^2/g] be the surface area of powder per unit of mass. Let us assume that the flow of gas through the powder bed can be equivalent of gas flow through imaginary **N** capillaries of the same radius **R** and the length of the powder bed height **h**. Therefore, the total area of capillaries walls can be calculated as :

$$S_a \cdot m_b = 2 \cdot \pi \cdot R \cdot h \cdot N \quad \text{(Eq. 1)}$$

where $\mathbf{m_b}$ is the mass of the powder bed. Since S_a, R, and N are unknowns, additional two equations are needed. The flow $\mathbf{f_c}$ through a single capillary is described by Poisseuille equation and its corrected version for compressible fluids (gases) will be used.

$$\text{Total Flow } F = N \cdot f_c = \frac{N \cdot \pi \cdot R^4}{16 \cdot \mu \cdot h P_o} \cdot \left(P^2 - P_o^{\,2}\right) \quad \text{(Eq. 2)}$$

where $\boldsymbol{\mu}$ is the dynamic viscosity, **P** is the pressure at the bed input, $\mathbf{P_o}$ is pressure at the bed output. Both sides of the equations are multiplied by N since experimentally we can only measure the total flow through all capillaries. An important consequence of this equation is that both pressure values, P and P_o must be known, not just a difference between the two as in incompressible fluids case. In most typical experiments the P_o is just the atmospheric pressure but in general case, the P_o can be of any

value, from vacuum to much higher pressures then atmospheric. If Po can be controlled from vacuum to high pressures and the same flow rate is ensured, then various P-Po differences will be obtained, which cannot be explained by equations derived for incompressible fluids.

A packed bed of powder can be perceived as a sum of two volumes, one occupied by the sample and another one called void volume consisting of empty spaces between and intra-particles throughout the bed. To provide some idea about the amount of void volume $\mathbf{V_v}$ in a given powder bed, the dimensionless quantity, $\boldsymbol{\epsilon}$, called bed porosity is defined as ratio of void volume and geometrical volume of the bed $\mathbf{V_b}$.

$$\epsilon = V_v/V_b = \frac{V_b - V_p}{V_b} = 1 - \frac{V_p}{V_b} \quad \text{Eq. 3.}$$

where the $\mathbf{V_p}$ is the bed volume determined from gas (helium) pycnometer measurements. Although it is feasible to design a special version of instrument that allows all the measurements to be carried out in the same sample chamber, it is far more common to separately determine the density of powder from which the bed is formed. Knowing the powder density and the mass of the powder used for the bed formation, the V_p can be easily obtained by dividing the mass of the bed by the powder density.

The third equation that is needed for determining the unknowns S_a, N, and R can be proposed by stipulating that cross-sectional area of all N capillaries, each of radius R, should be equal the powder bed area $\mathbf{A_b}$ multiplied by the porosity factor ϵ.

$$\pi \cdot R^2 \cdot N = A_b \cdot \epsilon \qquad \text{Eq. 4.}$$

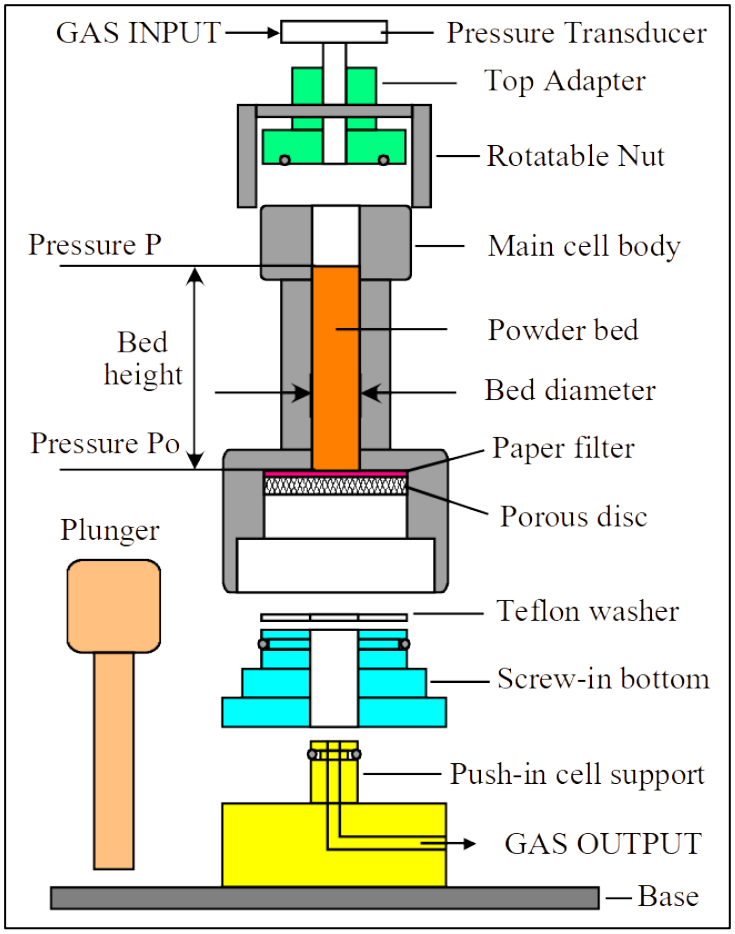
This seems reasonable as the gas can flow only through the voids. Solving the equations 1, 2, and 4 yields the S_a value expressed only by measured quantities and it can be presented in one of the possible forms below:

$$S_a = \frac{A_b}{2 \cdot m_b} \cdot \sqrt{\frac{\epsilon^3 \cdot V_b \cdot (P^2 - P_o^2)}{\mu \cdot P_o \cdot F}} \quad \text{Eq. 5}$$

Sa – specific surface area [cm^2/g]
A_b –geometrical surface area of the powder bed [$cm^{2]}$
m_b – mass of the powder used for bed formation [g]
ϵ – bed porosity [dimensionless]
V_b – geometrical volume of the powder bed [cm^3]
P – pressure at the top of the powder bed [kPa]
Po – Pressure at the bottom of the powder bed [kPa]
μ – dynamic viscosity [Pa·s]
F – flow rate [cm^3/min]

Since no additional factors were introduced in this derivation, this equation can be considered absolute. It can be used for any powder and does not require any reference materials as in comparative approaches. Having obtained the S_a value, the other quantities like R and N can be obtained.

To facilitate measurements of the powder density and gas transport rates through various barriers, a more complex design of a volumetric analyzer, pV/T Master, and auxiliary hardware was undertaken. The sketch of a general-purpose permeability cell is presented below.



Sketch of the permeability cell for measurement of gas flow through various barriers

The permeability cell consist of several easy to assembly components and it is to be used as a standalone structure, external to the core instrument. The lower part of the main cell body can accept various barriers that can be used for measurement of gas flow rates through them. Once the particular barrier is installed, the bottom of the cell can be screwed in to provide support for the barrier. Once the barrier is fastened, the top adapter adapter needs to be connected to the top threaded part to provide gas input and connection to pressure transducer. The whole assembly can be pushed into the cell support block. The gas output from the block can be redirected either to a gas flow measurements calibration device, to a vacuum pump, or to an appropriate exhaust. Connecting the gas output to a bubble flow meter and using a digital stopwatch, the correction factor can be obtained for various gases used.

Once the setup is ready, the prepared in software protocol can be started and the experiment carried out automatically. The experimental data are recorded in the text format for any further processing. Using a mass flow controller of 500 cc/min flow rate, the flow rates from just above 2% to 100% are available. The pressure range depends on the particular type of pressure transducer used and on the set pressure value, typically about 1-2 bar above atmospheric pressure.

In case of measurements of flow rates through packed bed of powder, the particular construction of the support for such bed will depend on the fineness of the powder. Using a circle (18-20 mm diameter) of paper filter, let say 8 microns or lower, and a metal support disc of porosity let say 20 or 40 microns, will form a sufficient barrier for many powders. Once the particular bed support is constructed, the selected flow rate(s) can be applied to asses the flow resistance through such barrier without any powder sample there. This pressure at a selected flow rate will be the **P_o** value.

To form the powder bed, the main cell body with the support and bottom adapter attached need to be removed from the measuring station. The measured diameter of the cylindrical bore where the bed will be formed is the diameter of the bed **d_b**. Before forming the bed, it is a good idea to determine the depth of the well as it will be useful after the bed is formed. One way is to insert the plunger into the well and use a good quality caliper to measure the distance from the bottom of the cell to the top of the plunger as shown on the photo below. Let the measured value be **h_1**.

Next step would be to weigh the empty cell using an analytical balance and let the recorded mass be **m_1**. Using an appropriate funnel, fill the cell with either a certain mass of the DRY powder or to some height, e.g. 10 -15 mm below top edge. Inserting very slowly the plunger into the cell and pressing it down will form the bed. It is a very important step and it can affect the results if is not done right. It is recommended to hold the plunger down while applying vibrations from the bottom to let the powder settle in tightly. The plunger can be turned somewhat and pressed down and repeat the process several times to form a flat bed. Once it is done, the distance between the plunger top and the cell bottom needs to be measured again, and let it be **h_2**. The difference between h_2 and h_1 yields the bed height **h**.

After the height measurement, the plunger should be removed very slowly from the cell. Any residual powder that is not part of the bed should be cleaned. The cell with the formed bed should be reweighed and let the recorded mass be **m_2**. Obviously, the difference between the m_2 and m_1 is the mass of powder bed **m_b**. Now attach the top adapter to the cell and slowly push the assembly onto the cell

support bloc. It is assumed that the connections to gas supply port and the pressure transducer are already done and the special adapter is already installed in the pV/T Master sample chamber. The picture below shows the permeability cell setup prepared for gas flow measurements.

What is left it to just start the experiment using the prepared template for permeability applications. The run with the powder bed will yield the flow rate F and the pressure P. If the powder density has not been done before, then it needs to be done now using the pV/T Master as a pycnometer. Having all the data collected, the user may can utilize the specific surface area calculator included in the software to obtain the S_a value. Alternatively, any other theoretical model can be tried using the obtained data.

It should be clearly understood, that such parameter as specific surface are is only a calculated number that is highly dependent on the theoretical model and particular technique used, sample preparation, instrumentation, and other factors. This novel implementation of the permeametry technique offers quick and convenient way of carrying out of automatic measurements using rather a simple and inexpensive equipment. Plurality of applications can be addresses where various powders need to be researched for specific purposes. Correlating specific surface area obtained by this method with results obtained by other methods would increase popularity of this approach. One of the advantages of the permeametry method is that data are obtained in a more realistic conditions of temperatures, pressures, and gases that can be found in actual applications. The “active sites” of highly cleaned samples and available for adsorption at liquid nitrogen temperature where high surface area in BET method can be obtained are not necessarily available in real conditions. In addition to characterizing powders, measuring flow resistance through easily permeable barriers increases applicability of such equipment. Since the permeability station is remote to the main instrument, it can be placed in different temperature environments and provide valuable data for the studied materials.

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