

## **A Study of Specific Surface Area for Matrix, Eheim Substrat Pro, and JBL MicroMec**

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### **Abstract**

BET surface area measurements indicate that Matrix contains nearly 10 times the specific surface area of Substrat Pro, and more than 20 times the specific surface area of MicroMec. Practically all the specific surface area of both Substrat Pro and MicroMec are in the range of pore diameters to be biologically useful, while some of the surface area of Matrix is in pores that are reserved for physical and chemical processes, not biological processes. Estimates from two different pore geometries indicate that Matrix contains between 4 to 4 ½ times the biologically active surface area of Substrat Pro, and between 8 to 9 times the biologically active surface area of MicroMec.

### **Introduction**

Seachem Laboratories sells Matrix, a natural porous stone, as a biological filter medium. Two competitors, Eheim (Substrat Pro) and JBL (MicroMec) are advertising their own biological filter media (in both cases, sintered glass) and are claiming larger specific surface areas than our claim for Matrix.

For biological filter media, specific surface area (measured as surface area per gram of material, or surface area per some specified volume of material) is very important. These products provide surface sites for bacteria to attach and do their work. The greater the surface area per gram of medium, the greater the number of bacteria that can attach. Thus a high specific surface area is desirable.

There is a second consideration, and that is the size of the pores in the medium. Generally, with very large pore diameters, we have smaller specific surface area, so that is not good. This generally rules out pores above 10 microns in diameter. But we can go too far in the other direction. If we have a very large number of very, very small pores, then our specific surface area number will be phenomenal, but the medium will not work very well as a biological medium. This is due to physical limitations, specifically too small a volume to support bacterial growth, and the decreasing efficiency of fluid transport (necessary to carry nutrients to the bacteria and waste away from the bacteria) with very small pore sizes. (Small pores still play important roles in physical and chemical processes, such as adsorption.)

So it behooves us to look at both the specific surface area, and the distribution of pore diameters (distribution because the pores will most definitely not be uniform.)

## BET Adsorption

The BET adsorption isotherm is a theoretical construct that has been around since 1938, when Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published their paper on the subject (see the reference section, Brunauer *et al.*). For those of you with an historical interest, the Edward Teller who co-authored this paper is the Edward Teller who, just four years later, would attend what was in essence the organizational meeting for the Manhattan Project. He moved to Los Alamos in 1943, and worked diligently on the world's first nuclear fusion weapon. He is often referred to as the "Father of the Hydrogen Bomb."

The BET theory is not terribly complicated, but we are not required to know much about it to appreciate its role in determining specific surface area. In fact, one author summed it up quite nicely:

"Although it is now generally agreed that the BET Theory was based on an over-simplified model of physisorption, the BET-nitrogen method continues to be used as a standard procedure for the determination of the surface area of fine powders and porous materials. There are probably two main reasons for its continued popularity: first, under favorable conditions, the BET plot does appear to provide a fairly reliable estimate of the monolayer capacity – especially for nitrogen adsorption at 77K; secondly, the method is not difficult to apply or comprehend." (Sing)

Or, to put it in a slightly more scientific manner:

"Of equal significance is the fact that in the region of relative pressures near completed monolayers ( $0.05 \leq P/P_0 \leq 0.3$ ) the BET theory and experimental isotherms do agree very well, leading to a powerful and extremely useful method of surface area determination. (Lowell *et al.*)

The versatility, and the accuracy, of the BET method continues to amaze, some 70 years after its development. For example, a recent paper attempted to establish the accuracy of the BET method for a new class of porous materials, called metal-organic frameworks (MOFs). These materials displayed very large BET surface areas, and two researchers undertook the rigorous task of comparing BET data with calculations from the crystal structures. These two researchers concluded:

"BET surface areas calculated from the simulated isotherms agree very well with the accessible surface areas calculated directly from the crystal structures in a geometric fashion. In addition, the surface areas agree well with experimental reports in the literature. These results provide a strong validation that the BET theory can be used to obtain surface areas of MOFs." (Walton and Snurr)

We thus feel quite comfortable using BET nitrogen adsorption isotherm data to characterize specific surface area.

## Mercury Porosimetry

The equation that provides the foundation for the mercury porosimetry technique was developed and refined in 1805 and 1806 (Young, Laplace), and the first operating instrument was reported in 1945 (Ritter and Drake). The idea behind the method is easy to explain because the equation of Young and Laplace is easy to explain:

$$D = 4\gamma\cos\theta/P$$

Where  $D$  is the diameter of the pore in the porous material,  $\gamma$  is the surface tension of the liquid, being used,  $\cos\theta$  is the cosine of the contact angle that the liquid makes with material being tested, and  $P$  is the pressure applied to the liquid. We want to find  $D$ , so we force liquid mercury (which has a surface tension  $\gamma$  that we can either look up in a textbook or measure very quickly, and forms a contact angle  $\theta$  that can be looked up in a textbook or measured very quickly, and which usually runs around 130 to 140 degrees) under pressure  $P$  into the solid and we measure the volume of mercury taken up. That is all we have to do (aside from making some assumptions about the shape of the pores, for the geometry to work properly.) It is that simple. At different pressures, we force mercury into different size pores, so we can obtain a distribution of pore sizes. The process then becomes a calculation exercise, based on our geometric assumptions.

Which means that it isn't the very last word in accuracy. There are some assumptions in this very simple procedure that we know are not correct. For one thing, the method assumes that the capillaries that are absorbing the mercury are all the same shape, and we know that isn't true. They have a variety of shapes, and some have several different shapes at once. We assume that the substrates being tested are stiff, which is true in the case of our study, but not true in the case of, say, fabrics (Nagy and Vas). The effects of compression can cause problems when the method is used for substrates that can be destroyed, such as pharmaceutical tablets (Westermarck).

Still, with all the imperfections of the method, it has remained in continuous use for decades. It is perhaps best used to compare similar substrates, given that the errors that affect one will affect the other, and thus not enter into the picture. We will use mercury porosimetry to compare pore size distributions of the three media, and in the case of specific calculations, we will use ratios to cancel out errors.

## Experimental

BET specific surface areas and mercury porosimetry distributions of pore diameter were determined at Micromeritics Analytical Services in Norcross, Georgia. For all three samples, BET bath temperature was 77.300 degrees Kelvin. All samples were degassed for four hours at 473.15 degrees Kelvin. The instrument used for the analysis is a TriStar 3000 V6.08 A.

Porosimetry data were collected with an AutoPore IV 9500 V1.07 scanning mercury porosimeter. Mercury contact angle was taken as 130 degrees, and surface tension was entered as 485 dynes/cm.

## Results

The BET-nitrogen specific surface area results are listed in the table below:

Sample	BET Surface Area m <sup>2</sup> /g	Apparent Density g/L	BET Surface Area m <sup>2</sup> /L
Matrix	2.1172	752	1592
Substrat	0.2171	656	142
MicroMec	0.1051	888	93

Apparent density is the mass, in grams, of one liter of medium. We poured each medium into a graduated cylinder to the 500 ml mark, weighed the material in the cylinder on a top-loading balance, and then multiplied the mass by two. This is the density that is useful to the hobbyist: it is the specific surface area one can expect when the proper volume of medium is measured in a volumetric measuring device, such as a measuring cup or graduated cylinder.

We note at this point that the conversion from area in meters squared per gram to meters squared per liter is an opportunity for misunderstanding. There are several different densities that can be used. We have used the density that will be most meaningful to the hobbyist. One may use the actual density of the material itself: i.e., the mass of one sphere of sintered glass divided by the volume of that sphere. This will, of course, result in a higher density than that obtained by the method used above. The mercury porosimeter calculates two different densities, one called a bulk density, one a skeletal density. Both are higher than the apparent density as measured above. For example, for the Eheim Substrat Pro, we measure an apparent density of 656 g/L. The porosimeter yields a bulk density of 1190 grams per liter, and a skeletal density of 2307 grams per liter. These higher densities are densities one would expect to obtain if the Substrat Pro were manufactured in the form of a one liter block, with no air voids between particles to lower the effective density.

The following table shows the effect of density on BET surface area of Eheim Substrat Pro.

Density	BET Surface Area, m <sup>2</sup> /L
Apparent	142
Bulk	258
Skeletal	501

The specific surface area of this product, as listed on the box, is very close to the value we calculate using the skeletal density.

The difficulty in determining the useful value of density is not restricted to the hobbyist. Industries that deal with compressible materials (rubber, textiles, paper) have great difficulty in measuring a value of density that is relevant. And although we have settled on a method that makes sense to us, there is room for error in that method. For example, how tightly do we tamp the product down in the graduated cylinder? What tamping pressure do we use?

It seems clear to us that the hobbyist would be better served were specific surface areas reported in units of square meters per gram. This would avoid the question of density measurement completely. But for historical reasons, densities are used to convert the units of BET surface area from square meters per gram, to square meters per liter. As the table above demonstrates, the conversion can yield numbers that vary widely.

The mercury porosimetry graphs showing the distribution of pore diameters are shown below. The y-axis is the log differential intrusion in ml/g, or  $dV/d\log D$ , where  $V$  is the volume of mercury intruded into the pores of the sample. As you can see, this is the derivative of intruded volume with respect to the logarithm of pore diameter. The derivative with respect to  $\log D$  is used instead of the derivative with respect to  $D$  when we want to amplify the  $dV/dD$  values for  $D$  greater than about 2 microns. The derivative plot has the virtue of clearly identifying points of inflection, which in this case shows us where clusters of pores of a particular diameter occur.

Figure 1. Log Differential Intrusion vs. Pore Size for Matrix

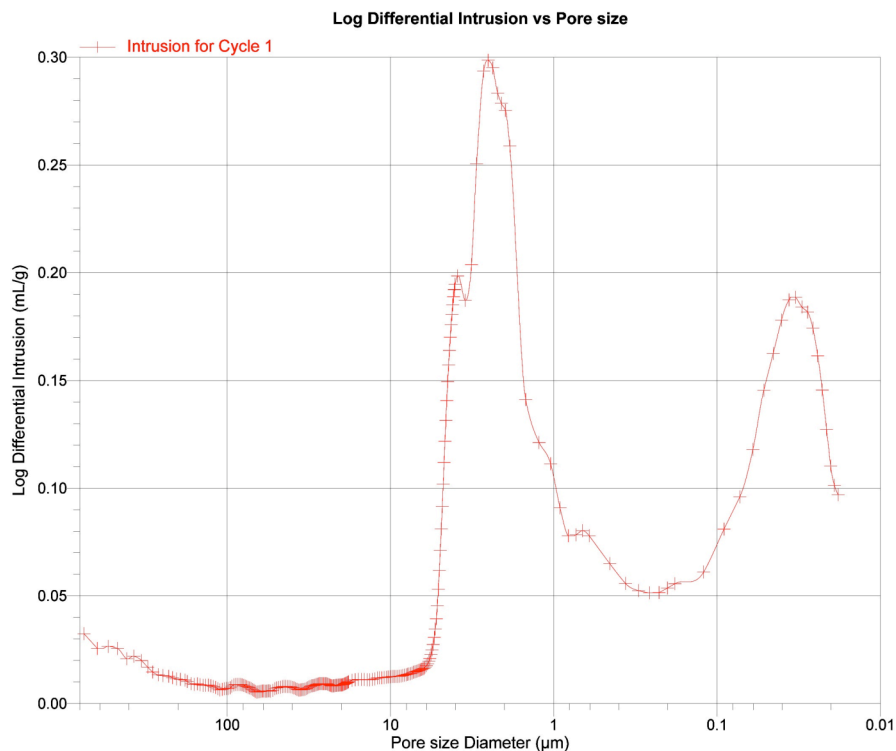


Figure 2. Log Differential Intrusion vs. Pore Size for Substrat Pro

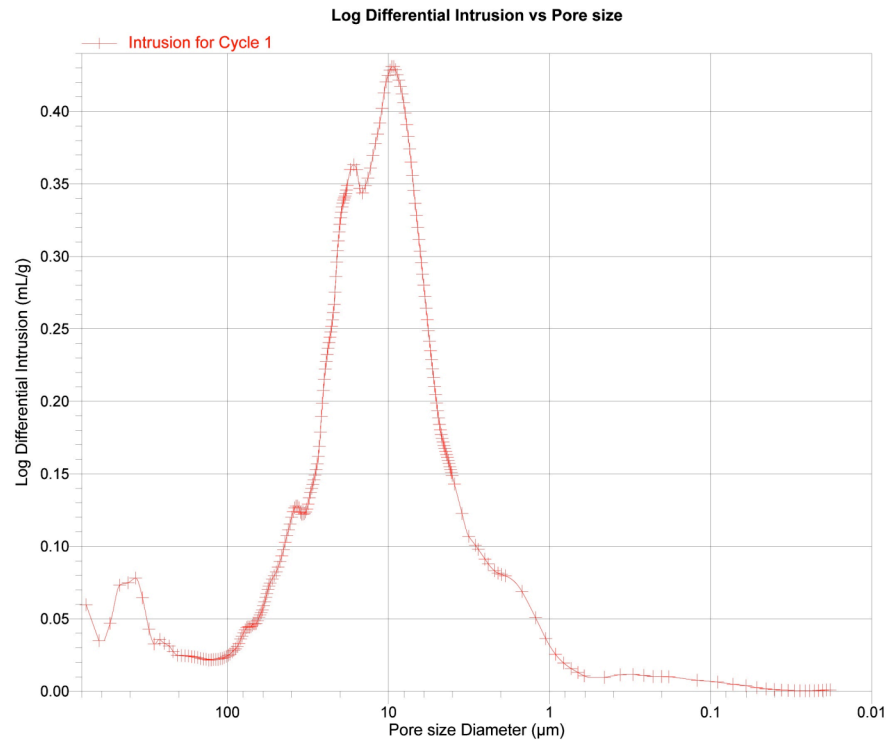
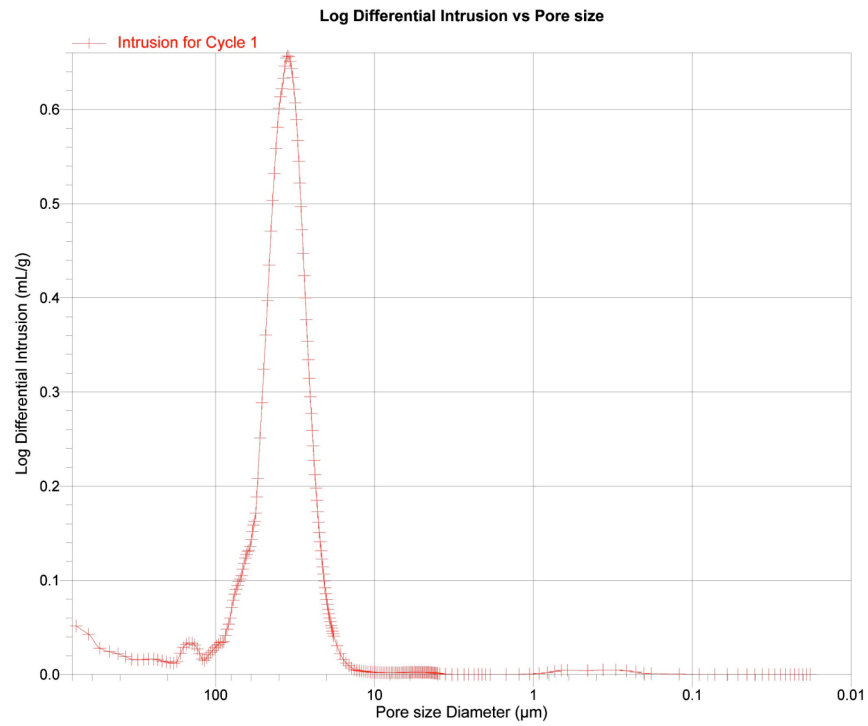


Figure 3. Log Differential Intrusion vs. Pore Size for MicroMec



The first thing we notice when reviewing the figures is that the Matrix plot is the only bimodal plot of the three. This means that Matrix has a cluster of pore diameters in the range of 1 to 8 microns (remember that the x-axis is logarithmic), and another cluster in the range of 0.02 to 0.10 microns.

Substrat Pro yields a fairly broad, single peak in the range of 4 to 13 microns. Given that the x-axis is logarithmic, the peak is broader than it appears in the plot. By contrast, the MicroMec plot has a single peak that appears to be fairly narrow, but is in fact extremely broad, in the range of 20 to 60 microns.

These results are consistent with the BET surface area data. We know that there is an inverse relationship between pore diameter and specific surface area, and we see that in these data. The MicroMec product shows the greatest diameter pores, and the smallest BET surface area. Matrix shows the smallest set of pore diameters under the second peak of the log differential intrusion plot, and the highest BET surface area. The Substrat Pro is between the other two, both in pore diameters and BET surface area.

The question of interest, with respect to the bimodal Matrix distribution, is how much of the total surface area is consumed by pore diameters below 0.4 microns, and therefore not useful from a biological perspective? We can determine this from the porosimetry volume data, and from the graph.

The porosimetry data for Matrix give a total intrusion volume of 0.3331 mL/g (or  $3.331 \times 10^{-7}$  m<sup>3</sup>/g). Since the graph is just differential volume plotted against pore diameter, then the integral of this with respect to pore diameter should give the intrusion volume for any portion of the curve. This integration is accomplished very easily once we recognize that the result of the integration is just the area under the curve. So, if we measure the total area under the curve, then measure the area under the curve from 0.4 microns and below, we will have an excellent idea of the fraction of total volume consumed by the small pores below 0.4 microns.

A larger copy of the log differential volume plot for Matrix was photocopied onto 24 pound copy paper. The area under the entire curve was then cut out with scissors, and weighed. The result was 0.334 g. Another cut with the scissors produced the portion of the area that arose from pore diameters of 0.4 microns and less. This section of the curve weighed 0.133 g. This means that  $0.133/0.334 = 0.3982$  (or 39.82%) of the total volume was consumed by the pores of 0.4 microns or less.

In order to obtain the portion of the total area consumed by the pores of various sizes, we must make assumptions regarding the geometry of the pores. We can examine two different geometries in order to obtain limits. If we assume that all the pores are spherical, then our surface area is proportional to the 2/3 power of volume:

$$A \propto V^{2/3} \text{ for spherical pores.}$$

For cylindrical pores, surface area is proportional to the 3/5 power of volume:

$$A \propto V^{3/5} \text{ for cylindrical pores.}$$

The relationship between area and volume for the spherical pores is probably obvious, but the relationship for cylindrical pores is most likely not obvious. We explain both, as follows.

For a sphere, we have the following formulae:

$$\begin{aligned} V &= 4/3\pi r^3, \\ A &= 4\pi r^2. \end{aligned}$$

To obtain area, which goes as  $r$  squared, from volume, which goes as  $r$  cubed, we take the  $2/3$  power of volume, so that  $r^{3(2/3)} = r^2$ .

For cylinders, the volume is  $\pi r^2 h$ , while the surface area is  $2\pi r h$ , where  $h$  is the height of rise of the mercury in the cylindrical column. But  $h$  is related to  $r$ . Early in the last century, two physicists working independently on the equation of Young and Laplace derived and solved an equation for the penetration of a liquid in a cylindrical capillary (Lucas, Washburn). Their equation, and the solution for capillaries, can be found elsewhere (Batten). For our purposes it is sufficient to note that the height of rise of a liquid in a capillary,  $h$ , is proportional to the square root of  $r$ :

$$h \propto r^{1/2} \text{ for cylinders.}$$

This means that, for cylinders,

$$V \propto r^{5/2}, \text{ and } A \propto r^{3/2}, \text{ so } A \propto V^{3/5} \text{ for cylindrical pores.}$$

We can now estimate that portion of the total surface area that is in pores of 0.4 microns or less in diameter. Total intrusion volume was  $3.331 \times 10^{-7} \text{ m}^3/\text{g}$ , and 39.82 % of that volume was in pores of 0.4 microns diameter or smaller, or  $1.326 \times 10^{-7} \text{ m}^3/\text{g}$ , so the fraction of surface area in the small pores is:

$$(1.326 \times 10^{-7})^{2/3} / (3.331 \times 10^{-7})^{2/3} = 0.5412 \text{ for spherical pores; and}$$

$$(1.326 \times 10^{-7})^{3/5} / (3.331 \times 10^{-7})^{3/5} = 0.5755 \text{ for cylindrical pores.}$$

This implies that, for spherical pores, 45.88% of the surface area is biologically useful, while for cylindrical pores, 42.45% of the surface area is biologically useful. With that in mind, we re-examine the first table in this paper:

Sample	BET Surface Area, $\text{m}^2/\text{g}$
Matrix	2.1172
Matrix, biologically useful, spherical pores	0.9714
Matrix, biologically useful, cylindrical pores	0.8988
Substrat Pro	0.2171
MicroMec	0.1051



It would appear from the estimates based on idealized geometry, that specific surface area is proportional to volume raised to some power less than one. These two extremes, perfectly spherical pores, and perfectly cylindrical pores, result in two exponents that are fairly close (0.60 vs. 0.66).

Although the surface area that is taken up in pores too small to be biologically useful is a little more than half the total, Matrix still has available for biological processes a greater surface area than either Substrat Pro or MicroMec.

## **Conclusions**

BET surface area measurements indicate that Matrix contains nearly 10 times the specific surface area of Substrat Pro, and more than 20 times the specific surface area of MicroMec. Practically all the specific surface area of both Substrat Pro and MicroMec are in the range of pore diameters to be biologically useful, while some of the surface area of Matrix is in pores that are reserved for physical and chemical processes, not biological processes. Estimates from two different pore geometries indicate that Matrix contains between 4 to 4 ½ times the biologically active surface area of Substrat Pro, and between 8 to 9 times the biologically active surface area of MicroMec.

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