Counterpoint: The microporosity of pulp

The importance of being accessible[1]

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The classical challenge of defining the total porous structure of water swollen fibers has been recognized for more than 20 years *(1)*. However, in terms of our new concept of micropackaging or entrapment of materials within cellulosic fibers, the important relevant information is the **accessible** not the true pore volume *(2)*.

The nature of this accessible pore distribution was discussed in our second paper in the series dealing with the unutilized microporosity of pulp *(3)*. Here, it was concluded that the **apparent accessible pore** volume followed a log-normal distribution for a wide variety of cellulosic materials. The approach leading to this conclusion did not require any assumptions as to the size and shape of the **true pores.**

Based on this finding, the evaluation of the accessible pore distribution can be obtained using only three measurements. A first measurement, utilizing a high molecular weight dextran (Dextran 24,000 for example) as the molecular probe, yields the total pore volume. Two other similar measurements with lower molecular weight materials, such as glucose and Dextran 150, allow the accessible pore volume to be determined for each of the solute probes. These data then enable the percentage cumulative pore volume for the two low molecular weight chemicals to be computed. When plotted on a log-normal function graph, the straight line linking the two points obtained describes the accessible pore volume distribution for the fibers in question. This straight line permits the accessible pore volume available for another solute of known size to be conveniently estimated. An example of this procedure is shown in **Fig. 1** for the case of a bleached pine sulfite pulp and a solute having a molecular diameter of 100 Å. This analysis suggests that this solute could access 30% of the total pore volume. The amount of this particular substance which would be entrapped within the fibers can therefore be readily predicted.

A possible shortcoming of such an analysis, however, lies in the extrapolation from the results obtained with such "sugars" to other chemically distinct compounds. The specific interactions between the pulp and the new solute, as well as the concentration of this solute, in the solution might affect the observed accessible pore volume. These limitations are felt to be the only real problems in the practical utilization of this technique.

Accordingly, it is not germane that a knowledge of the true size and shape of the pores in cellulosic fibers would allow the evaluation of a partition of solutes within those pores. Unfortunately, the actual pore geometry is not available and only **assumed** shapes and sizes can be used. Furthermore, from the description of Alince's approach, it is obvious that the pores these referred to are the **true pores** and not the **observed accessible pores** considered by

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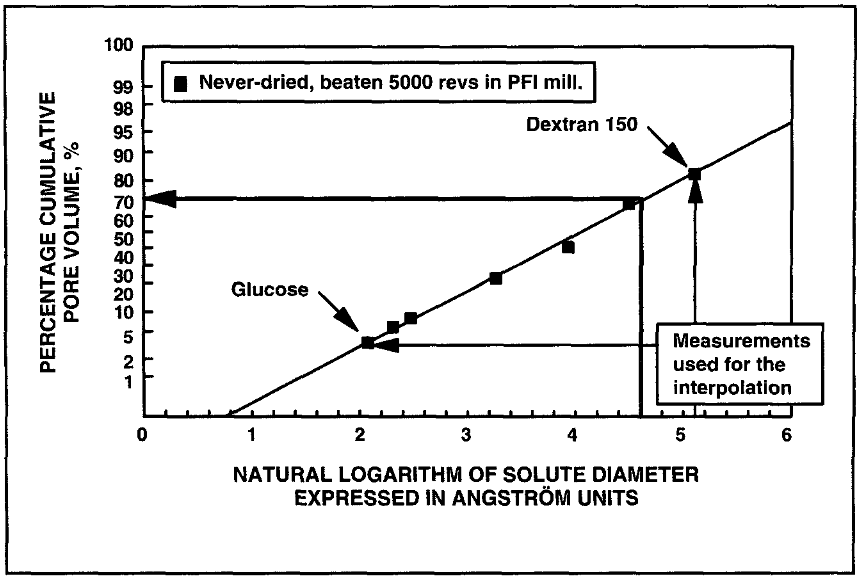
Allan, Ko, and Ritzenthaler *(3)*. The latter, of course, are those of practical interest for entrapment experiments.

Finally, Alince's interesting analysis has the same intrinsic weakness as the approach taken by Allan *et al.* in predicting the penetration of various materials into the pores of even a well-characterized material because the effect of the solution of this solute on the porous structure is not firmly known. Moreover, Alince's assumption of an idealized cylindrical pore shape does not seem judicious for pulp because of the reported presence of "lamellar ink-bottle" shaped pores *(6)*.

Thus today, the precise nature of the actual pores in cellulosic fibers still remains unknown and the determination of the true pore distribution would inevitably require a more elaborate approach than the one taken by Day, Alince, and Robertson *(7)* with its assumption of an idealized pore shape. Notwithstanding these unresolved questions, the useful accessibility of solutes within the pores of cellulosic fibers can clearly be determined without serious doubt from a limited number of measurements using the log-normal distribution approach taken by Allan, Ko, and Ritzenthaler *(3)*. This approach is valid regardless of the true size and shape of the pores in cellulosic materials.

1. Evaluation of the percentage of the pore volume in a bleached pine sulfite pulp inaccessible to a solute having a diameter of 100 Å [original data from *(4, 5)*].



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