## Selecting the Appropriate Minimum and Maximum Thickness Values for Micropore t-Plots

The selection of appropriate minimum and maximum thickness values for t-plots is a very important factor in the determination of micropore volume. This application note briefly describes the t-plot method, - explains why the thickness values are so important, and offers some suggestions for determining minimum and maximum values that will produce the best results. The instructions refer to Micromeritics Surface Area software.

Description of t-Plot Method

The t-plot method can be used to determine the micropore capacity (volume) of solids even when both micropores and mesopores are present. Adsorption initially occurs in micropores in order to satisfy their excess potential energy originating from an overlapping of energy fields from the walls of the pores. After the micropores are filled, mesopores begin filling as the relative pressure increases.

Thus, a combination of Type I and Type IV adsorption isotherms is obtained. Total pore volume can be estimated from the maximum uptake of gas (V) at $P/Po \approx 1$ (refer to Figure 1).

Figure 1
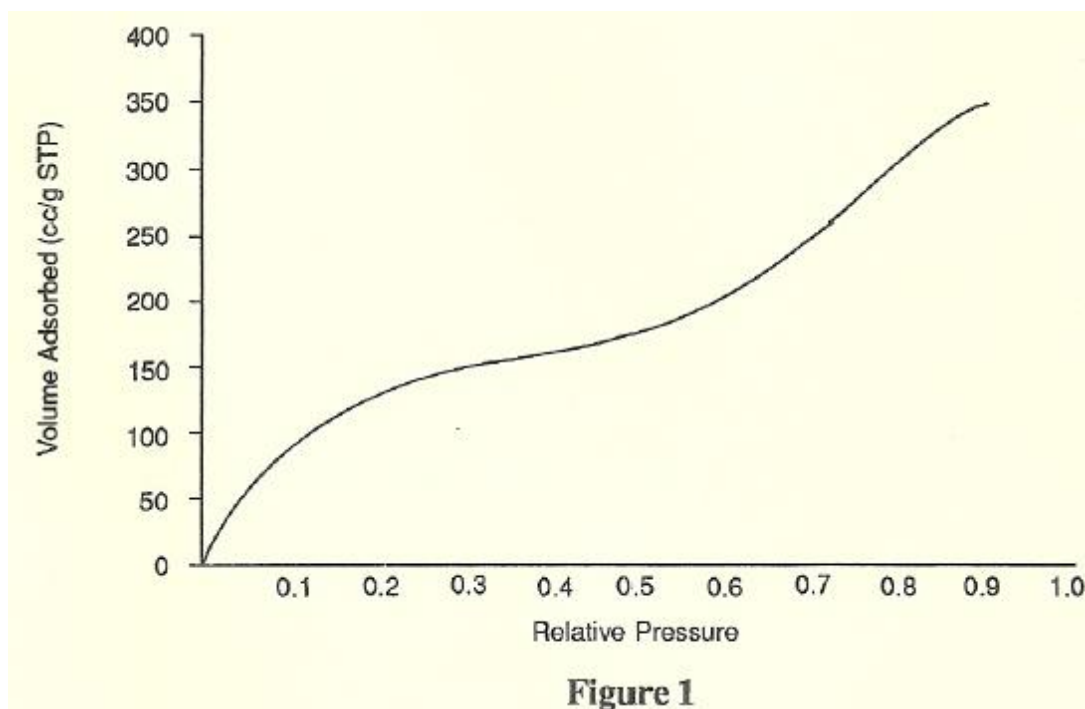
Using the isotherm provided by the analysis program, the t-plot
method differentiates between micropores and mesopores,thus,yielding
an estimate of micropore volume. Because micropores are filled at
very low relative pressure, the lower the relative pressure the
better the distribution profile and representation of the t-curve.
Thus, starting adsorption at the lowest possible value of relative
pressure is advisable. A high vacuum system is also very important.

Why the Minimum and Maximum Values for Thickness are Important
A t-curve is the graphical representation of the uptake of gas,
expressed in cm_3/g, at certain equilibrium pressures as a function of
the statistical thickness of the adsorbed film at corresponding
pressures. The -statistical thickness(represented as **t**) of the
adsorbate film within a pore is calculated using either the Halsey[1]
equation or the Harkins and Jura[2] equation.

A curve, such as that shown in Figure 2, is obtained for the t-plot,
where point (1) represents an inflection point at the intersection of
the two tangents drawn across the two portions of the t-curve. Point
(1) indicates a complete filling of micropores and the beginning of
mesopore filling. A tangent (2) drawn correctly across the flat
portion (plateau) of the t-curve will determine the micropore volume
when it is extrapolated to the Y-axis. **Any two points taken from the
portion of the curve where the tangent and the plateau coincide can
be used to determine the limits for t**. A perpendicular line from each
point to the X-axis determines the two values (minimum and maximum)
of **t**. Thus, in the example shown in -Figure 2, the minimum and
maximum values can be from 8 to 16 Angstroms (Å).

When these two values of **t** are entered in the report option,a new
t-plot curve is obtained and a tangent is drawn correctly across the
plateau and extrapolation to the Y-axis is then constructed. At this
time, a certain volume of gas adsorbed is shown as micropore volume
when it is converted to equivalent volume of liquid as follows:

$$Vgas \ (cm3/g \ STP) \ x \ 0.0015468 = Vliquid$$
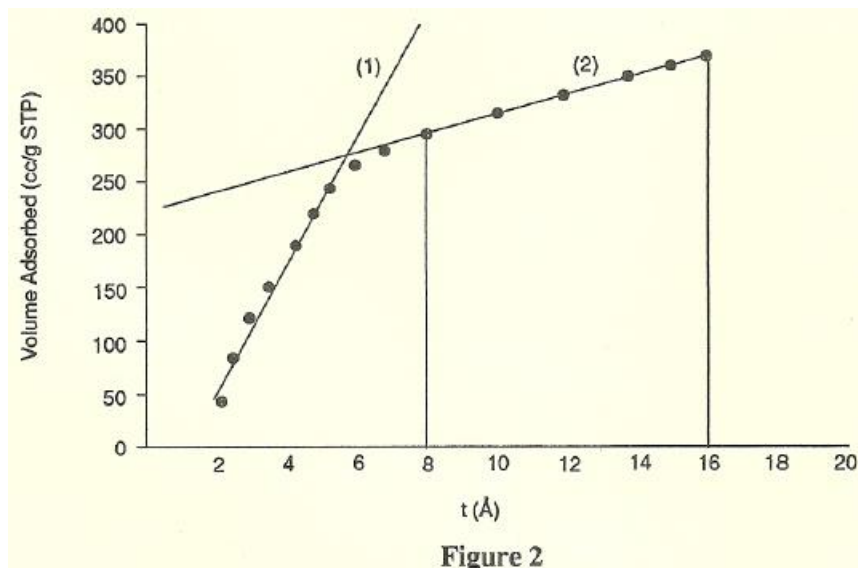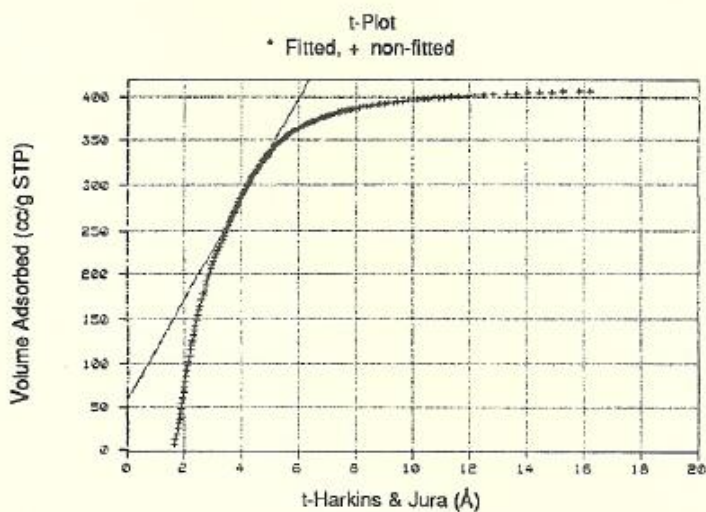

Figure 2

The following illustrations show the importance of selecting appropriate t-value limits and their influence on micropore volume determination. Figures 3 and 4 show the t-plots produced by entering inadequate values for minimum and maxmum thickness. Figure 5 shows the t-plot produced by entering adequate t-values.
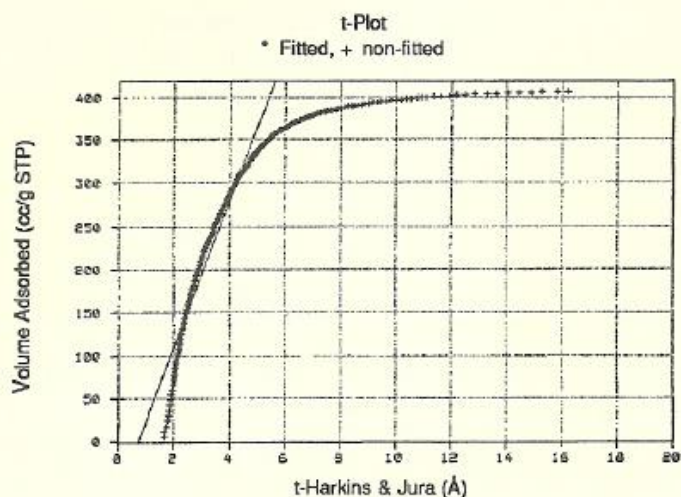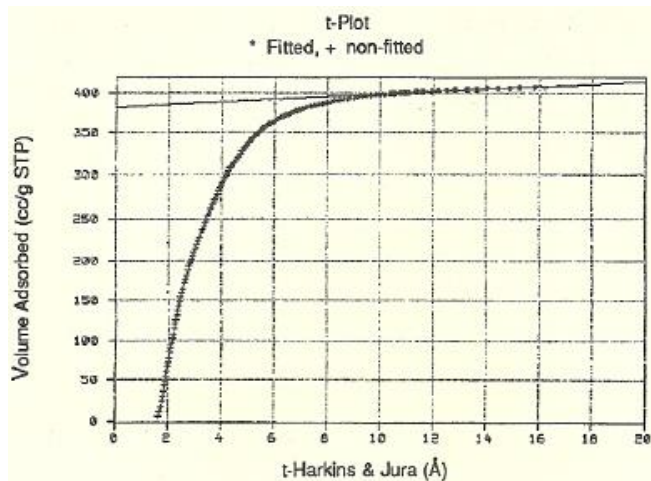

Entered minimum thickness = 2.0 Å
Entered maximum thickness = 5.0 Å
Micropore volume obtained = -0.075 cm^3/g

Figure 3

Entered minimum thickness = 3.5 Å
Entered maximum thickness = 5.0 Å
Micropore volume obtained = 0.076 cm^3/g

Figure 4

t-Plot
* Fitted, + non-fitted

Entered minimum thickness = 10.0 Å
Entered maximum thickness = 16.0 Å
Micropore volume obtained =   0.488 cm^3/g

Figure 5

As you can see from the figures above, Figure 3 gives a negative micropore volume for a microporous solid. This case indicates that the limits for t were incorrectly selected at the low range of the t-curve where micropores were not completely filled yet. Figure 4 gives a positive micropore volume but much smaller than the expected volume for a microporous solid. The limits of t-selected in this case underestimated by far the true micropore volume because the slope of the tangent is still too high.

Figure 5 reflects the correct micropore volume because the tangent was drawn across the plateau of the t-curve. The micropore volume calculated in this case is 6.5 times higher than the volume obtained in Figure 4. Figure 3 gives completely unacceptable results, that is, a negative micropore volume for a microporous solid. The correct selection of t-limits makes a great difference when determining micropore volume.

How to Select Appropriate Minimum and Maximum Thickness Values

1. Create a t-plot that includes at least 15 points in the low range of relative pressures as shown in Figure 6. Select either the **Halsey** or **Harkins and Jura** equation (from the t-Plot Report screen, you may toggle between these fields by pressing ⑤ on the numeric keypad).

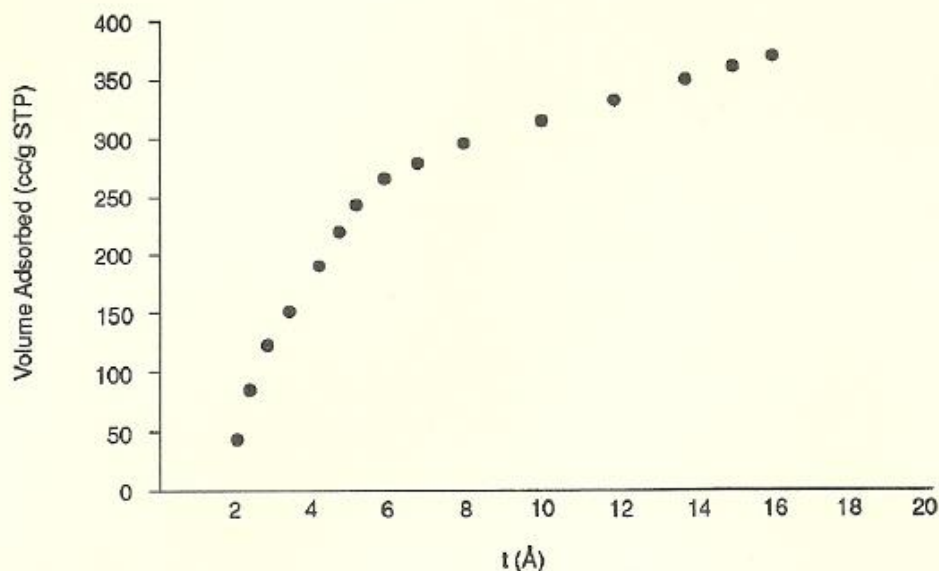2. Print a copy of the t-plot after the analysis is finished.

Figure 6

3. Use a ruler to draw a tangent that coincides with the flat section (plateau) of the t-curve.
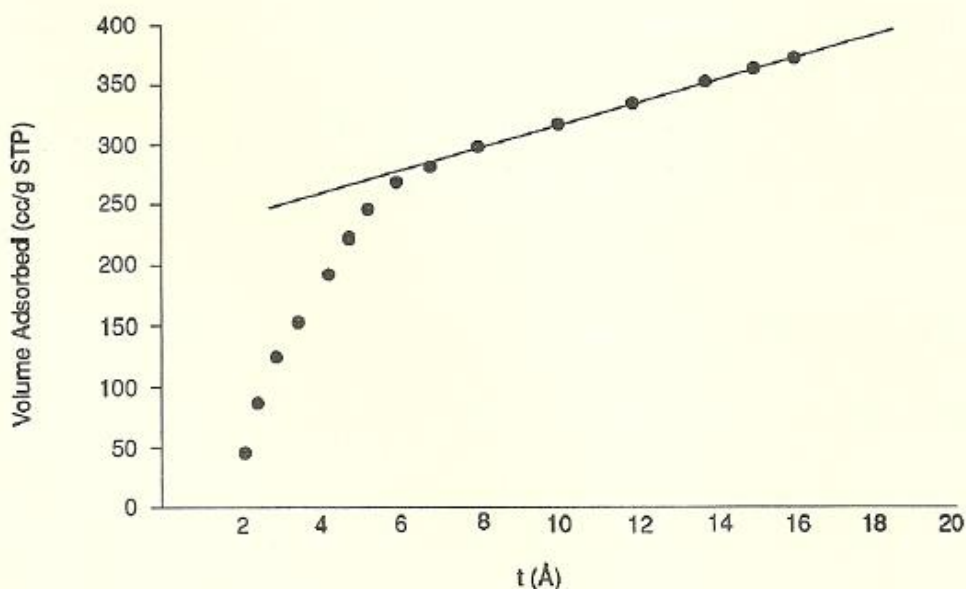

Figure 7

4. Select any two points on this tangent in the portion where tangent and curve coincide. Usually, the first point is taken at one end of the line and the second at the other end of the line. From the two points, draw two lines perpendicular to the X-axis to determine the minimum and maximum values of thickness in Angstroms. In the example, the minimum and maximum values are 8 and 16 Å.
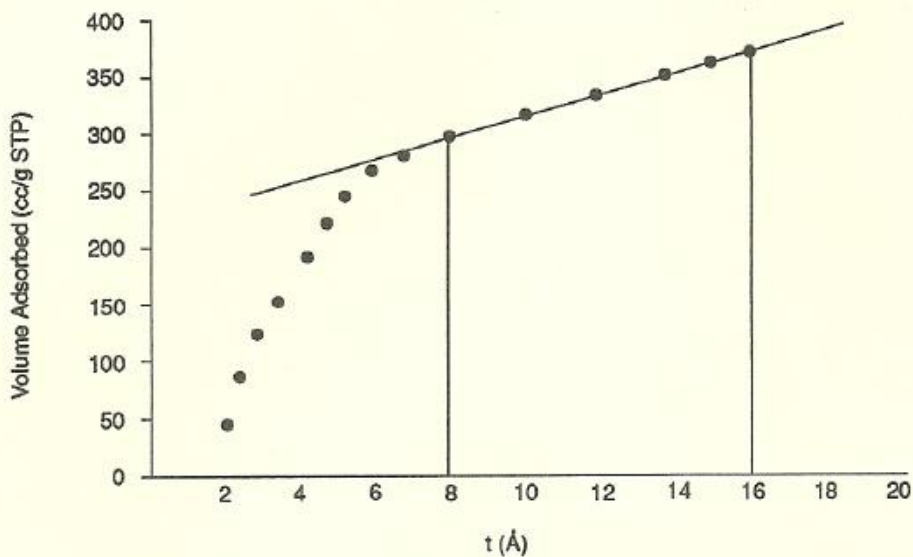

Figure 8

Entre com os novos valores para recalcular e salve as alterações.

5. Enter the new values of t in the analysis program as follows:

   - Press **F3** from the Main Function Menu to display the Sample Information Menu.
   - Press **F4** to display the Change Sample Information screen.
   - Enter the sample number, then press **PgDn** until the Report Options screen is displayed.
   - Press **F8** to display the t-Plot Report screen.
   - Enter the corrected values for minimum and maximum thickness.
   - Press **PgDn** twice to return to the Main Function Menu.

6. Press **F6** **F3** to display the Start Report screen. Select t-Plot if it is not already selected, then press **PgDn** to start a report that will give the correct value for micropore volume.