Quantachrome
INSTRUMENTS

AUTOSORB AS-3B & AS-6B

MULTISTATION GAS SORPTION SYSTEM

USERS MANUAL

Models:	AS-6B, AS-6B-Kr
	AS-3B, AS-3B-Kr
Firmware:	ver 2.55 (AS-6B), ver 3.26 (AS-3B)
PC Software:	ver 1.23

P/N 05063 Rev F

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AUTOSORB

CALIBRATION DATA

Calibration Sphere Volume 56.5592 cm^3

Model Number ____________

Serial Number _____________

QUANTACHROME WARRANTY POLICY

Quantachrome Instruments warrants its instruments to be free from defects in material and workmanship for a period of one year from date of shipment under normal use and conditions.

For the period commencing with the date of shipment and ending one year later, Quantachrome will, at its option either repair or replace any part within an instrument that is found by us to be defective in material or workmanship, without charge to the customer, at our facility or at a customer's facility if the instrument purchased is backed by Quantachrome's on-site warranty as evidenced by the sales contract.

The customer is responsible for all transportation charges to our factory.

Damages during the warranty period resulting from unstable utilities, operator error or unauthorized repairs will not be covered by this warranty.

Parts purchases are warranted to be free of defects for 90 days from shipping date.

The following limits apply to our warranty:

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Warranty becomes void in the event of modifications or repairs by persons other than Quantachrome's service personnel, unless permission is given in writing for such repairs or modifications. Warranty is also void in the event of exposure to corrosive atmospheres of any kind.

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Payment terms: Terms are net 30 days from date of invoice for established accounts where Seller has received adequate financial information to warrant extending credit to Buyer. Purchase orders from customers not meeting with Seller's financial approval are not accepted under credit terms.

Delivery: Delivery dates are Seller's best estimate of the time products will be shipped from our factory and we assume no liability for loss, damage, or consequential damages due to delays. No liability shall result from delay in performance or non-performance of this agreement, directly or indirectly caused by fire, explosion, accidents, flood, labor trouble or shortage, war, act of God or arising from contingencies, happenings, or causes beyond the control of the party affected.

Material Shortages: In the event of inability for any reason to supply the total demands for the materials specified in this order, Seller may allocate its available supply among any or all purchasers, as well as departments and divisions of the Seller, on such basis as it may deem fair and practical, without liability for any failure or performance which may result there from.

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Changes: Orders accepted by the Seller cannot be changed or modified in whole or part, except with the written consent of Seller.

Return Policy: Prior approval must be obtained from an authorized Seller representative to return any Product. Seller will assign a return authorization number and record the reason for return. Seller will examine returned part to determine the actual cause, if any, leading to Buyer's return. If Product has a manufacturing defect Seller will, at its discretion, repair or replace with like product.

Restocking charges: Product purchased, under the sole discretion of the Seller, may be returned for a 20% restocking fee and must be returned within 90 days of date of delivery. Product cannot be returned if used or modified.

Claims: Claims for shortages or damage must be reported within 10 business days after receipt of shipment. All claims for loss or damage in transit must be made against the carrier.

Warranty: Quantachrome Instruments warrants all instruments that it manufactures for a period of twelve months from the date of delivery. This warranty includes all parts and labor. Quantachrome does not warrant any product against damage from corrosion, contamination, misapplication, improper specification, or wear and tear and operational conditions beyond the Seller's control. This warranty excludes all glassware and expendable items associated with each instrument. Repairs made during the warranty period are guaranteed until the end of the warranty period or 90 days, whichever is greater.

CAUTION

HEATING MANTLES, SAMPLE CELLS AND CLAMPS CAN BECOME VERY HOT AND CAUSE INJURY OR DAMAGE IF NOT PROPERLY HANDLED

Never handle hot mantle, cells or clamps with your bare hands.

Do not use in the presence of flammable or combustible materials.

Keep hot mantles clamps and cells at least 3 inches from combustible surfaces at all times.

Hot heating mantles, clamps and cells must always be placed on a heat resistant surface. When filling dewar flask with liquid nitrogen care must be taken to prevent LN_2 from getting between the glass insert and the outer cover. This can cause the glass to implode.

Because the dewar flask can shatter unexpectedly, a protective shield, safety glasses, and gloves should be worn when filling the flasks.

Hot heating mantles, clamps and cells must always be placed on a heat resistant surface

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I. INTRODUCTION

The AUTOSORB operates by measuring the quantity of gas adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressure by the static volumetric method. The data are obtained by admitting or removing a known quantity of adsorbate gas into or out of a sample cell containing the solid adsorbent maintained at a constant temperature below the critical temperature of the adsorbate. As adsorption or desorption occurs the pressure in the sample cell changes until equilibrium is established. The quantity of gas adsorbed or desorbed at the equilibrium pressure is the difference between the amount of gas admitted or removed and the amount required to fill the space around the adsorbent (void space).

The AUTOSORB has the capability of measuring adsorbed or desorbed volumes of nitrogen at relative pressures in the range 0.001 to slightly under 1.0. When the krypton and micropore options are added, the lower limit is extended and data points can be requested at $1x10^{-5}$. This volume-pressure data can be reduced by the AUTOSORB software into BET surface area (single and/or multipoint), Langmuir surface area, adsorption and/or desorption isotherms, pore size and surface area distributions, micropore volume and surface area using an extensive set of built-in data reduction procedures.

The Quantachrome AUTOSORB Software interfaces the AUTOSORB to a computer for data acquisition, reduction and archiving.

A. SUMMARY OF FEATURES

- Menu-driven, easy-to-use software allows user to collect, display, analyze and archive data.
- User-configurable defaults simplify operations and offer flexibility in customizing reports and plots.
- Plots of data generated on-screen for quick preview or printed for archival purposes.
- The PC is used as an intelligent terminal for control of the AUTOSORB.
- Any or all data/reports can be saved to disk enabling data archiving.
- During a run, each data point can be acquired and saved to the data file so that in the event of an error condition, data that has been acquired will not be lost.
- User-defined analysis files enable flexible and easy operation of the AUTOSORB.
- The PC is used to review the archived data.
- Not copy-protected.

B. NOTATION USED IN THIS MANUAL

This manual refers to keystrokes or commands in UPPER CASE characters surrounded by <angle brackets>. When asked to type something at the keyboard, type only what is surrounded by the angle brackets <>. The <ENTER> key, the function keys <F1> through <F10>, <ESC>, <CTRL>, <NUM LOCK>, and the <BREAK> keys are exceptions. Instead of typing the word ENTER, press the ENTER key. For example, if the manual indicates typing <TEST> <ENTER>, type the word TEST and press the ENTER key. Do not type the angle brackets.

Selections made with a mouse are denoted by square brackets [OPERATIONS].

II. THEORY

The various theories for surface area and porosity measurements are discussed below.

A. SURFACE AREA

$$\frac{1}{W\left(\left(P_0/P\right)-1\right)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right) \qquad (1)$$

The Brunauer-Emmett-Teller (BET) method[1] is the most widely used procedure for the determination of the surface area of solid materials and involves the use of the BET equation (1). in which W is the weight of gas adsorbed at a relative pressure, P/P_0, and W_m is the weight of adsorbate constituting a monolayer of surface coverage. The term C, the BET C constant, is related to the energy of adsorption in the first adsorbed layer and consequently its value is an indication of the magnitude of the adsorbent/adsorbate interactions.

1. MULTIPOINT BET METHOD

The BET equation (1) requires a linear plot of $1/[W(P_0/P)-1]$ vs P/P_0 which for most solids, using nitrogen as the adsorbate, is restricted to a limited region of the adsorption isotherm, usually in the P/P_0 range of 0.05 to 0.35. This linear region is shifted to lower relative pressures for microporous materials. A typical BET plot is shown in Figure II-1.

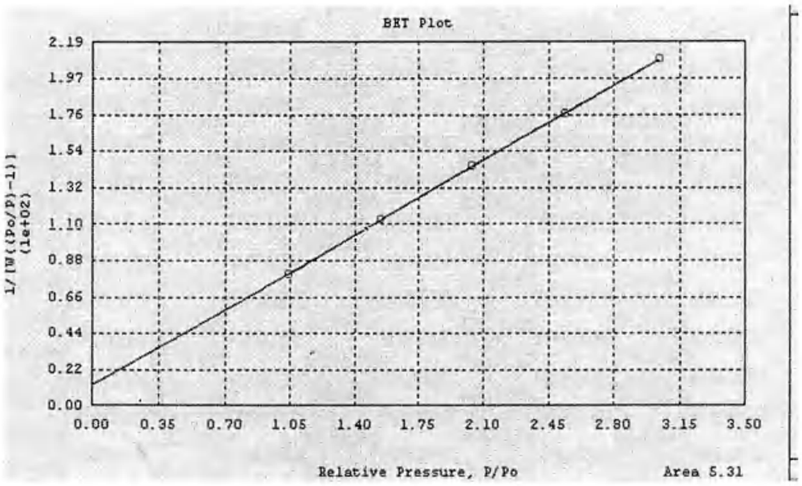


Fig. II-1. Typical BET plot.

$$s = \frac{C-1}{W_m C} \tag{2}$$

The standard multipoint BET procedure requires a minimum of three points in the appropriate relative pressure range. The weight of a monolayer of adsorbate W_m can then be obtained from the slope s and intercept I of the BET plot. From equation (1):

$$i = \frac{1}{W_m C} \tag{3}$$

Thus, the weight of a monolayer W_m can be obtained by combining equations (2) and (3).

$$W_m = \frac{1}{s+i} \tag{4}$$

The second step in the application of the BET method is the calculation of the surface area. This requires a knowledge of the molecular cross-sectional area A_{cs} of the adsorbate molecule. The total surface area S_t of the sample can be expressed as:

$$S_t = \frac{W_m \ N \ A_{cs}}{M} \tag{5}$$

where N is Avogadro's number (6.023×10^{23} molecules/mol) and M is the molecular weight of the adsorbate. Nitrogen is the most widely used gas for surface area determinations since it exhibits intermediate values for the C constant (50-250) on most solid surfaces, precluding either localized adsorption or behavior as a two dimensional gas. Since it has been established[2,3] that the C constant influences the value of the cross-sectional area of an adsorbate, the acceptable range of C constants for nitrogen makes it possible to calculate its cross-sectional area from its bulk liquid properties. For the hexagonal close-packed nitrogen monolayer at 77 K, the cross-sectional area A_{cs} for nitrogen is 16.2 Å^2.

$$S = S_t / w \tag{6}$$

The specific surface area S of the solid can be calculated from the total surface area S_t and the sample weight w, according to equation (6):

2. SINGLE POINT BET METHOD

$$W_m = W(1 - P/P_0) \tag{7}$$

For routine measurements of surface areas a simplified procedure may be applied, using only a single point on the adsorption isotherm in the linear region of the BET plot. For nitrogen the C value is usually sufficiently large to warrant the assumption that the intercept in the BET equation is zero. Thus, the BET equation (1) reduces to

$$W_m = \frac{PVM}{RT}\left(1 - P/P_0\right) \tag{8}$$

By measuring the amount of nitrogen adsorbed at one relative pressure (preferably near $P/P_0 = 0.3$) the monolayer capacity W_m can be calculated using equation (7) and the ideal gas equation. That is,

$$S_t = \frac{PVNA_{cs}\left(1 - P/P_0\right)}{RT} \tag{9}$$

The total surface area then can be obtained from equation (5). That is,

3. MULTIPOINT/SINGLE POINT COMPARISON

$$W_m = W\left(\frac{P_0}{P} - 1\right)\left[\frac{1}{C} + \frac{C-1}{C}\left(\frac{P}{P_0}\right)\right] \tag{10}$$

The relative error introduced by the single point versus the multipoint method for determining surface area is a function of the BET C constant and the relative pressure used. The magnitude of the error in the single point method can be determined from a comparison of the monolayer weight obtained from the BET equation (1) and the single point equation (7). Solving equation (1) for W_m gives:

$$W' = W\left[\left(P_0/P\right) - 1\right] P/P_0 \tag{11}$$

Rewriting the single point equation (7), gives

The relative error inherent in the single point method, then, is

$$\frac{W_m - W'm}{W_m} = \frac{1 - P/P_0}{1 + \left[P/P_0\left(C-1\right)\right]} \tag{12}$$

Equation (12) indicates that for a given C value, the relative error decreases with increasing relative pressure. Therefore, a relative pressure as high as possible, yet still in the linear region of the BET plot, should be chosen for single point surface area determinations. For all except microporous samples a P/P_0 of about 0.3 is preferable. For single point determinations on microporous samples a relative pressure as high as possible on the linear BET plot should be chosen.

Table I gives the relative error for various C values calculated from equation (13) using P/P_0 of 0.3. When the C constant is 100, a 2 percent error is indicated.

TABLE I

SINGLE POINT/ MULTIPOINT COMPARISON	
C CONSTANT	RELATIVE ERROR
1	0.70
10	0.19
50	0.04
100	0.02
1000	0.002
∞	0

$$C = (s/i)+1 \tag{13}$$

Prior to using the single point method for the determination of surface area, the C constant can be evaluated from a multipoint BET plot. That is,
where s and I are the slope and intercept, respectively, of the BET plot. Subsequently, the single point method can be used on materials having the same composition. For greater accuracy, if the C constant is known, the single point result may be corrected using equation (12).

C. POROSITY BY GAS ADSORPTION

It is expedient to characterize pores according to their sizes.

C. Pores with openings exceeding 500 Å in diameter are called “macropores”.
C. The term “micropores” describes pores with diameters not exceeding 20 Å.
C. Pores of intermediate size are called “mesopores”.

Porosity of powders and other porous solids can be conveniently characterized by gas adsorption studies. Two common techniques for describing porosity are the determination of total pore volume and pore size distribution. For the evaluation of the porosity of most solid materials, nitrogen at 77 K is the most suitable adsorbate.

C. ISOTHERMS

An understanding of the surface area and porosity of an adsorbent can be achieved by the construction of an adsorption isotherm. When the quantity of adsorbate on a surface is measured over a wide range of relative pressures at constant temperature, the result is an adsorption isotherm. The adsorption isotherm is obtained point-by- point on the AUTOSORB by admitting to the adsorbent successive known volumes of nitrogen and measuring the equilibrium pressure. Similarly, desorption isotherms can be obtained by measuring the quantities of gas removed from the sample as the relative pressure is lowered. All adsorption isotherms may be grouped into one of the five types shown in Figure II-2.

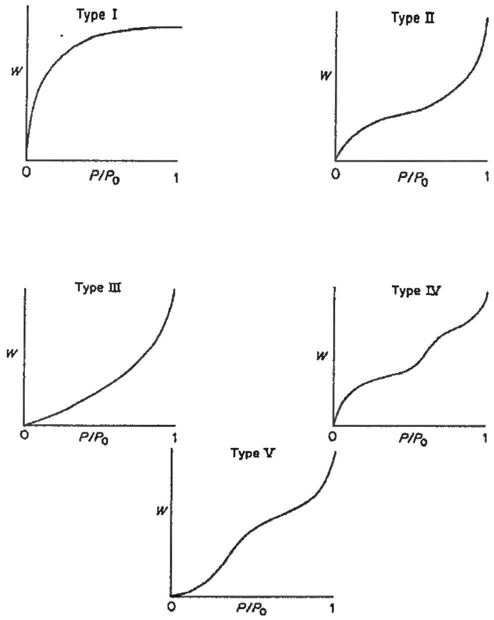


Fig. II-2 Isotherm types (classification by BDDT[4]).

Type I or Langmuir isotherms are concave to the P/P_0 axis and the amount of adsorbate approaches a limiting value as P/P_0 approaches 1. Type I physisorption isotherms are exhibited by microporous solids having relatively small external surfaces, for example, activated carbons and molecular sieve zeolites. The limiting uptake of adsorbate is governed by the accessible micropore volume rather than by the internal surface area.

Type II isotherms are the normal form of isotherm obtained with a nonporous or macroporous adsorbent. This type of isotherm represents unrestricted monolayer-multilayer adsorption. Point B, the start of the linear central section of the isotherm, is usually taken to indicate the relative pressure at which monolayer coverage is complete.

Type III isotherms are convex to the P/Po axis over its entire range. Type III isotherms are rarely encountered. A well-known example is the adsorption of water vapor on nonporous carbons. The absence of a distinct point B on type III isotherms is caused by stronger adsorbate-adsorbate than adsorbate-adsorbent interactions.

Type IV isotherms are associated with capillary condensation in mesopores, indicated by the steep slope at higher relative pressures. The initial part of the type IV isotherm follows the same path as the type II.

Type V isotherms are uncommon, corresponding to the type III, except that pores in the mesopore range are present.

Types I, II and III adsorption isotherms are generally reversible, but microporous materials having type I isotherms can exhibit hysteresis. Types IV and V, associated with mesoporosity, usually exhibit hysteresis between the adsorption and desorption isotherms. Points on the desorption isotherm are generated with the AUTOSORB by first adsorbing nitrogen on the solid surface at a relative pressure close to unity, then desorbing into an evacuated manifold, thus lowering the pressure to some value below ambient. This process is continued until sufficient points have been obtained to produce the desorption isotherm.

De Boer[5] has identified five types of hysteresis loops (Figure II-3) and correlated them with various pore shapes.

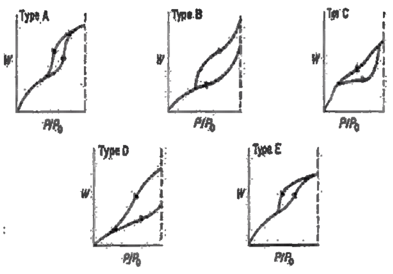


Fig II-3 de Boer's five types of hysteresis.

Type A hysteresis is attributed to cylindrical pores; type B is associated with slit-shaped pores; type C hysteresis is produced by wedge-shaped pores with open ends; type D loops result from wedge-shaped pores with narrow necks at one or both open ends. The type E hysteresis loop has been attributed to "ink-bottle" pores. Characteristically, the hysteresis loops in all isotherms close before reaching a relative pressure of 0.3 in the desorption process except when microporosity is present.

D. TOTAL PORE VOLUME AND AVERAGE PORE RADIUS

The total pore volume is derived from the amount of vapor adsorbed at a relative pressure close to unity, by assuming that the pores are then filled with liquid adsorbate. For a discussion of the relationship between pore size and relative pressure, see Section E. If the solid contains no macropores the isotherm will remain nearly horizontal over a range of P/P_0 approaching unity and the pore volume is well defined. However, in the presence of macropores the isotherm rises rapidly near $P/P_0 = 1$ and in the limit of large macropores may exhibit an essentially vertical rise. In this case the limiting adsorption can be identified reliably with the total pore volume assuming careful temperature control of the sample. The volume of nitrogen adsorbed (V_{ads}) can be converted to the volume of liquid nitrogen (V_{liq}) contained in the pores using equation (14).

$$V_{liq} = \frac{P_a \; V_{ads} \, V_m}{RT} \tag{14}$$

That is,
in which P_a and T are ambient pressure and temperature, respectively, and V_m is the molar volume of the liquid adsorbate (34.7 cm^3/mol for nitrogen).

$$r_p = \frac{2V_{liq}}{S} \tag{15}$$

Since pores which would not be filled below a relative pressure of 1 have a negligible contribution to the total pore volume and the surface area of the sample, the average pore size can be estimated from the pore volume. For example, assuming cylindrical pore geometry (type A hysteresis), the average pore radius r_p can be expressed as
where V_{liq} is obtained from equation (14) and S is the BET surface area. For other pore geometries a knowledge of the shape of the hysteresis in the adsorption/desorption isotherm is required.

E. PORE SIZE DISTRIBUTIONS (MESOPORE)

The distribution of pore volume with respect to pore size is called a pore size distribution. It is generally accepted that the desorption isotherm is more appropriate than the adsorption isotherm for evaluating the pore size distribution of an adsorbent. The desorption branch of the isotherm, for the same volume of gas, exhibits a lower relative pressure, resulting in a lower free energy state. Thus, the desorption isotherm is closer to true thermodynamic stability. In certain cases, for example, samples exhibiting type E hysteresis, the adsorption isotherm is recommended for pore size distribution determinations. The AUTOSORB offers the capability of using either branch of the isotherm for the calculation. Since nitrogen has been used extensively in gas adsorption studies, it has been well-characterized and serves as the most common adsorbate for pore size distribution measurements. Therefore, the following discussion will apply to the use of nitrogen as the adsorbate.

Mesopore size calculations are made assuming cylindrical pore geometry using the Kelvin equation (16) in the form

$$r_K = \frac{-2\gamma\ V_m}{RT\ \ln\left(P/P_0\right)} \tag{16}$$

where

γ = the surface tension of nitrogen at its boiling point (8.85 ergs/cm^2 at 77 K).
V_m = the molar volume of liquid nitrogen (34.7 cm^3/mol).
R = gas constant (8.314x10^7 ergs/deg/mol).
T = boiling point of nitrogen (77 K).
P/P_0 = relative pressure of nitrogen.
r_K = the Kelvin radius of the pore.

$$r_K\ (\text{Å}) = \frac{4.15}{\log\left(\,P_0/P\,\right)} \tag{17}$$

Using the appropriate constants for nitrogen, equation (16) reduces to
The Kelvin radius r_K is the radius of the pore in which condensation occurs at a relative pressure of P/P_0. Since, prior to condensation, some adsorption has taken place on the walls of the pore, r_K does not represent the actual pore radius. Conversely, during desorption an adsorbed layer remains on the walls when evaporation occurs. The actual pore radius r_p is given by

$$r_p = r_k + t \tag{18}$$

$$t\ (\text{Å}) = \left[\frac{13.99}{\log\left(P_0/P\right) + 0.034}\right]^{1/2} \tag{19}$$

where t is the thickness of the adsorbed layer. This statistical t can be considered as 3.54 (V_{ads}/V_m) in which 3.54 Å is the thickness of one nitrogen molecular layer and V_{ads}/V_m is the ratio of the volume of nitrogen adsorbed at a given relative pressure to the volume adsorbed at the completion of a monolayer for a nonporous solid of the same composition as the porous sample. A more convenient method for estimating t was proposed by de Boer[6] in the form of equation (19) and is accessible for pore size distribution calculations in the AUTOSORB software.

Other expressions for *t* calculations, available through the AUTOSORB software, are presented in the MICROPORE ANALYSIS section.

The AUTOSORB data reduction system computes the pore size distribution using the methods proposed by Barrett, Joyner and Halenda[7] (BJH) and by Dollimore and Heal[8] (DH).

1. BJH METHOD

$$V_{p1} = V_{K1}\, r_{p1}^2 / r_{K1}^2 \tag{20}$$

Assuming that the initial relative pressure $(P/P_0)_1$ is close to unity, all pores are filled with liquid. The largest pore of radius r_{p1} has a physically adsorbed layer of nitrogen molecules of thickness t_1. Inside this thickness is an inner capillary with radius r_K from which evaporation takes place as P/P_0 is lowered. The relationship between the pore volume V_{p1} and the inner capillary (Kelvin) volume V_K is given by

$$V_{p1} = V_1 \left(\frac{r_{p1}}{r_{K1} + \Delta t_1/2} \right)^2 \tag{21}$$

When the relative pressure is lowered from $(P/P_0)_1$ to $(P/P_0)_2$ a volume V_1 will desorb from the surface. This liquid volume V_1 represents not only emptying of the largest pore of its condensate but also a reduction in the thickness of its physically adsorbed layer by an amount Δt_1. Across this relative pressure decrement the average change in thickness is $\Delta t_1/2$. The pore volume of the largest pore may now be expressed as :

When the relative pressure is again lowered to $(P/P_0)_3$ the volume of liquid desorbed includes not only the condensate from the next larger size pores but also the volume from a second thinning of the physically adsorbed layer left behind in the pores of the largest size. The volume V_{p2} desorbed from pores of the smaller size is given by:

$$V_{p2} = \left(\frac{r_{p2}}{r_{K2} + \Delta t_2/2} \right)^2 \left(V_2 - V_{\Delta t_2} \right) \tag{22}$$

An expression for $V_{\Delta t_2}$ is

$$V_{\Delta t_2} = \Delta t_2\, Ac_1 \tag{23}$$

$$V_{\Delta t_n} = \Delta t_n \sum_{j=1}^{n-1} Ac_j \tag{24}$$

where Ac_1 is the area exposed by the previously emptied pores from which the physically adsorbed gas is desorbed. Equation (23) can be generalized to represent any step of a stepwise desorption by writing it in the form

$$V_{pn} = \left(\frac{r_{pn}}{r_{Kn} + \Delta t_n / 2} \right)^2 \left(\Delta V_n - \Delta t_n \sum_{j=1}^{n-1} Ac_j \right) \tag{25}$$

The summation in equation (24) is the sum of the average area in unfilled pores down to, but not including, the pore that was emptied in the desorption. Substituting the general value for $V_{\Delta t_2}$ into equation (22) results in an exact expression for calculating pore volumes at various relative pressures.

Since the area (Ac) for any one size empty pore is not a constant but varies with each decrement of P/P_0, this term must be evaluated.

$$A_p = \frac{2\, V_p}{r_p} \tag{26}$$

The area of each pore A_p is a constant and can be calculated from the pore volume, assuming cylindrical pore geometry. That is,

Then the pore areas can be cumulatively summed so that for any step in the desorption process A_p is known. The BJH method offers a means of computing $\sum Ac_j$ from A_p for each relative pressure decrement.

It is assumed that all pores emptied of their condensate during a relative pressure decrement have an average radius $\bar{r}_p$ calculated from the Kelvin equation (16) radii at the upper and lower values of P/P_0 in the desorption step. The average capillary (core) radius is expressed as

$$\bar{r}_c = \bar{r}_p - t_{\bar{r}} \tag{27}$$

where $t_{\bar{r}}$ is the thickness of the adsorbed layer at the average radius in the interval in the current pressure decrement and is calculated from equation (19).

$$c = \frac{\bar{r}_c}{\bar{r}_p} = \frac{\bar{r}_p - t_{\bar{r}}}{\bar{r}_p} \tag{28}$$

The term "c" in equation (24) then is given by

Equation (25) now can be used in conjunction with equation (28) as an exact expression for the computation of pore size distributions.

2. DH METHOD

A computationally simpler approach to evaluating mesopore size distributions was developed by Dollimore and Heal[8]. The DH approach differs from the BJH method in that the term $V_{\Delta t_n}$ in equation (24) is calculated from

$$V_{\Delta t_n} = \Delta t_n \Sigma A_p - 2\pi t_n \Delta t_n \Sigma L_p \qquad (29)$$

$$A_p = \frac{2 V_p}{r_p} \qquad \text{(cf. Eq. 26)}$$

where the summations ΣA_p and ΣL_p represent the areas and lengths, respectively, of all the pores emptied of condensate in previous desorption steps. Assuming cylindrical pore geometry, the cumulative pore areas and lengths can be estimated for each desorption step by summing the expressions
and

$$L_p = \frac{A_p}{2\pi r_p} \qquad (30)$$

respectively.

F. SURFACE AREA OF MICROPOROUS SAMPLES BY THE LANGMUIR METHOD

In the absence of meso and/or macropores, a sample containing micropores will exhibit a Type I or Langmuir isotherm (see Section C). The Langmuir equation (31) is a limiting case of the BET

$$\frac{W}{W_m} = \frac{C\,(P/P_0)}{1 + C\,(P/P_0)} \qquad (31)$$

equation (1) for the adsorption of a single molecular layer of adsorbate.

$$\frac{P/P_0}{W} = \frac{1}{CW_m} + \frac{P/P_0}{W_m} \qquad (32)$$

W and W_m are the weight of adsorbate at some P/P_0 and the weight in a monolayer, respectively. C is a constant associated with the energy of adsorption. Equation (31), rewritten in the form of a straight line

allows the determination of the slope ($1/W_m$) from a plot of $(P/P_0)/W$ versus P/P_0.

The weight of a monolayer W_m may then be used to calculate the total surface area of the sample from equation (5). This method is not applicable to composite materials containing both micropores and meso- and/or macropores.

G. MICROPORE ANALYSIS

Several different approaches to micropore analysis are available on the AUTOSORB. While no single treatment is applicable to all situations, enough flexibility is provided for the user to select the analysis most suitable for a given situation or material.

$$t\,(\text{Å}) = \left[\frac{13.99}{\log\left(P_0/P\right) + 0.034}\right]^{1/2} \qquad \text{(cf. 19)}$$

The AUTOSORB uses the t-method of Halsey[9], the generally preferred one of de Boer[10] or the CB (Carbon Black) method[11] for the determination of micropore volume in the presence of mesopores. This technique involves the measurement of nitrogen adsorbed by the sample at various low pressure values. The procedure is the same as that employed in the BET surface area measurement, but it extends the pressure range to higher pressures to permit calculation of the matrix or external surface area, that is, the non-microporous part of the material. A *t*-plot is a plot of the volume of gas adsorbed versus *t*, the statistical thickness of an adsorbed film. In the AUTOSORB the *t* values are calculated as a function of the relative pressure using either the de Boer equation,
the Carbon Black equation,

$$t_{CB}(\text{Å}) = 0.88\left(P/P_0\right)^2 + 6.45\left(P/P_0\right) + 2.98 \qquad (33)$$

$$t(\text{Å}) = 3.54\left[\frac{5}{2.303\,\log\left(P_0/P\right)}\right]^{1/3} \qquad (34)$$

or the Halsey equation which, for nitrogen adsorption at 77 K can be expressed as

$$t(\text{Å}) = a\left[\frac{1}{\ln\left(P_0/P\right)}\right]^{1/b} \qquad (35)$$

or in a generalized form (found useful for other adsorbates and/or temperatures) as
Where the pre-exponential term, a, and the exponential term, b, are 6.0533 and 3.0 for nitrogen adsorption at 77 K, respectively.

$$S_t = \frac{V_{ads}^{STP}\ (15.47)}{t\ (\text{Å})} \tag{36}$$

Typical *t*-plots are shown in Figures II-4, II-5 and II-6, representing various possible pore sizes. Figure II-4 is a *t*-plot of a sample having no micropores, as evidenced by the ability to extrapolate the line to the origin, since the slope represents the total surface area S_t of all the pores, that is, where V_{ads}^{STP} is the volume of gas adsorbed corrected to standard conditions of temperature and pressure and the constant 15.47 represents the conversion of the gas volume to liquid volume.

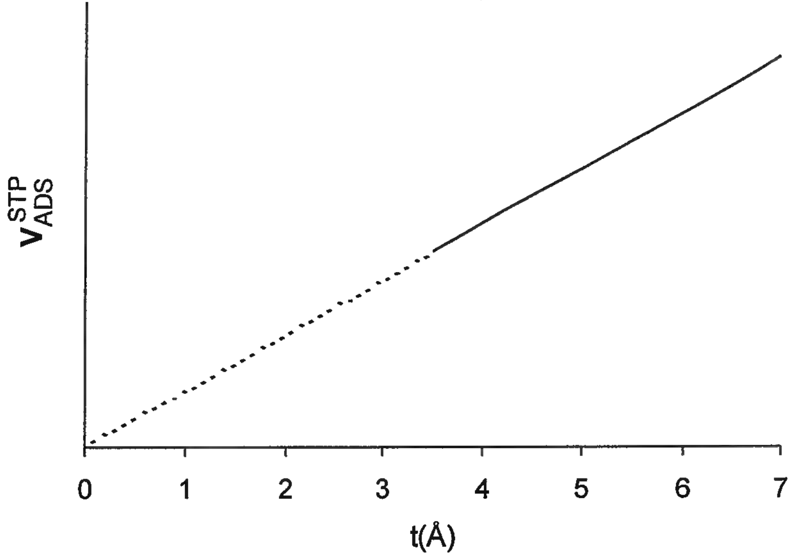


Fig. II-4. t-Plot of a mesoporous material.

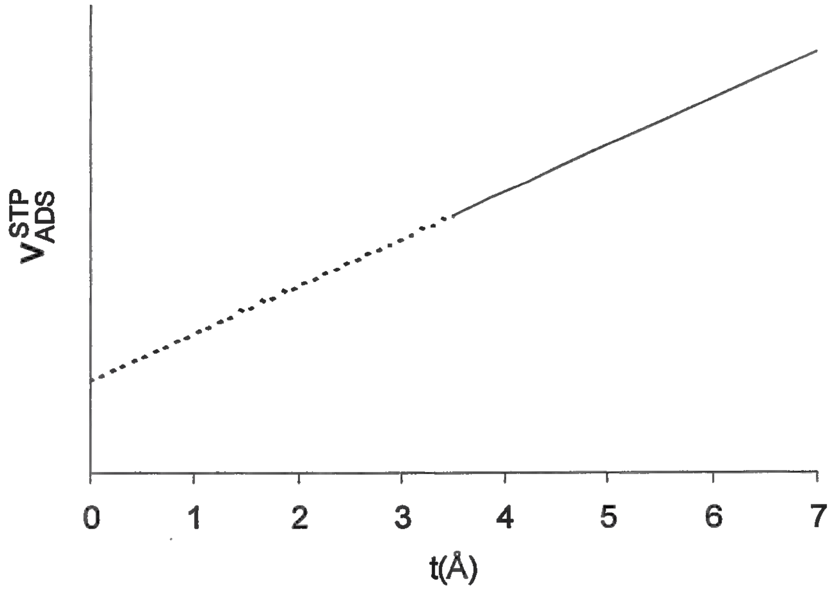


Fig. II-5. t-Plot of a microporous sample.

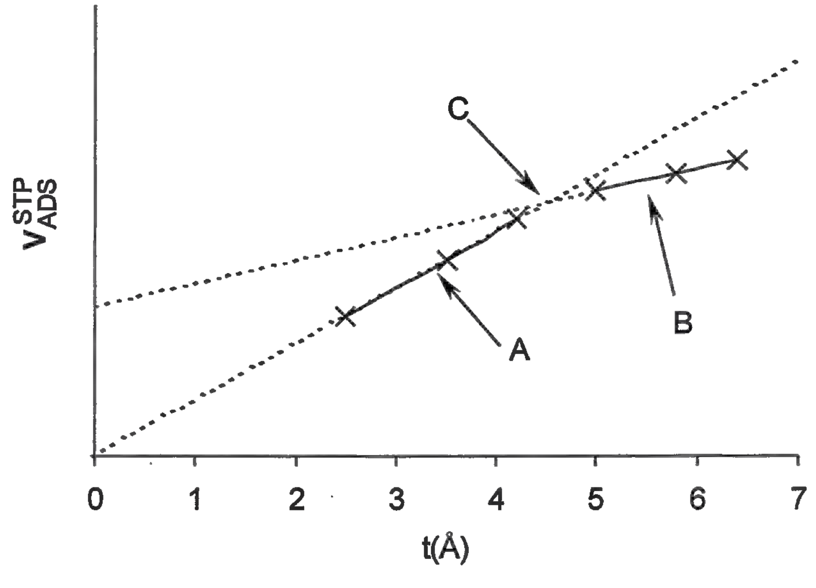


Fig. II-6. *t*-Plot of a microporous material.

Using the slope, s, of the plot in Figure II-4, equation (36) reduces to

$$S_t\left(m^2/g\right) = s \times 15.47 \tag{37}$$

In the absence of micropores there is good agreement between the *t*-area, S_t, and the surface area determined by the BET method.

$$V_{MP} = i \times 0.001547\left(cm^3\right) \tag{38}$$

When micropores are present the *t*-plot will exhibit a positive intercept. *t*-Plots for two types of microporous materials are shown in Figures II-5 and II-6. Figure II-5 is a t-plot of a sample with pore openings smaller than 7-8 Å diameter. Quantitative pore volume data from t-plots cannot be obtained below t=3.5 Å, corresponding to pores smaller than 7 Å wide, since this t value represents the diameter of a nitrogen molecule. The intercept, I, in the t-plot, when converted to a liquid volume, gives the micropore volume, V_{MP}. That is
The two linear regions of the t-plot in Figure II-6 indicate the presence of micropores larger than 7 Å and the actual pore width (2t) can be estimated at the position where the two linear plots intersect. The slope of the upper linear portion (B) of the *t*-plot in Figure II-6 gives the mesopore surface area using equation (34), while the slope of the lower linear portion (A) represents the total surface area of all pores. Point C indicates the presence of micropores of about 10 Å width (2t).

$$S_{MP} = S_{BET} - S_t \tag{39}$$

The linear BET region for microporous materials generally occurs at relative pressures lower than 0.1. The linear *t*-plot range will be found at higher relative pressures and is dependent on the size distribution of micropores. The micropore surface area, S_{MP}, then, is the difference between the BET surface area and the external surface area from the *t*-plot. That is,

1. BRUNAUER MP METHOD

$$t(\text{Å}) = \frac{V_{liq}}{S_{BET}} \times 10^4 \tag{40}$$

An extension of de Boer's *t*-method for micropore analysis was proposed by Mikhail, Brunauer and Bodor[12]. This MP method uses the fact that *t* can be calculated independently of the solid by
A V vs. *t* plot is constructed from *t* vs. P/P_0 data for a sample with a similar BET C value, as shown in Fig. II-7, using linear slopes constructed for *t*-value intervals from the origin to 4 Å, 4 to 4.5 Å. 4.5 to 5 Å, etc.

Using the equation above, micropore surface areas can be calculated from the slopes and each successive interval calculation represents the area of all the micropores remaining unfilled. The calculations are continued until no further decrease in slope is found in the V vs. *t* plot, indicating that all the micropores have been filled. The surface area of pores in the range of thickness from 4 to 4.5 Å, for example, is the difference between the values calculated from the first and second slopes. The area of pores in the thickness range from 4.5 to 5 Å is the difference between the values calculated from the second and third slopes, and so on.

$$V = 10^{-4}\left(S_1 - S_2\right)\left(\frac{t_1 + t_2}{2}\right) cm^3\ g^{-1} \qquad (41)$$

Pore volumes can similarly be calculated, using the relation
where S_1 = surface area calculated from slope 1
S_2 = surface area calculated from slope 2
t_1 = thickness at beginning of interval used for slope 2
t_2 = thickness at end of interval used for slope 2

Each succeeding group of pores is correspondingly treated, and a distribution of pore volume is thus obtained. While the exact pore shape is usually unknown, cylindrical pores are generally assumed. It has been shown that this pore volume relation is equally valid for cylindrical pores or parallel plates.

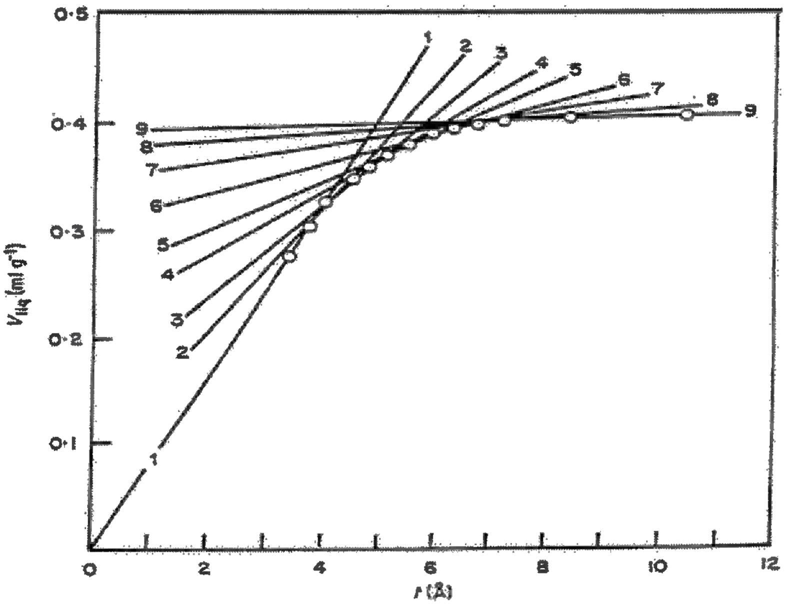


Fig. II-7. Typical V vs. t plot with interval slopes

2. DUBININ-RADUSHKEVICH (DR) METHOD

Based on the Polanyi potential theory of adsorption[13], Dubinin and Radushkevich[14] postulated that the fraction of the adsorption volume V occupied by liquid adsorbate at various adsorption potentials E can be expressed as a Gaussian function:

$$V = V_0 e^{-K(E/\beta)^2} \tag{42}$$

where

$$\beta = \frac{E}{E_{ref}} \tag{43}$$

K = a constant based on the pore size distribution shape
V = adsorption volume of liquid adsorbate
V_0 = adsorption volume of reference liquid adsorbate

$$E = RT\left(\ln\frac{P_0}{P}\right) \tag{44}$$

Since

$$\log W = \log(V\rho) - k\left(\log\frac{P_0}{P}\right)^2 \tag{45}$$

substitution and simplification yields

$$k = 2.303\,K\left(\frac{RT}{\beta}\right)^2 \tag{46}$$

where ρ = adsorbate liquid density, and

A plot of log W vs. $\left(\log \frac{P_0}{P}\right)^2$ gives a straight line with an intercept of log (Vρ), from which V, the micropore volume, can be calculated.
The Kaganer modification[15]

$$\log W = \log W_m - K'\left(\log\frac{P_0}{P}\right)^2 \tag{47}$$

allows a plot of log W vs. $\left(\log \frac{P_0}{P}\right)^2$ which yields a straight line intercept of log W_m, from which micropore surface area can readily be calculated (see equation 5). The linear range for these plots is usually found at relative pressures of less than 10^{-2}.

Other modifications[16] of the DR method include
(a) Allowing the DR exponent, n, to differ from n=2 in order to provide a better data fit for non-Gaussian pore size distributions - see section L; and

$$\log W = \log(V\rho) - k\left(\log K \frac{P_0}{P}\right)^2 \tag{48}$$

(b) introducing a supercritical adsorption constant, K, into equation (45)

where $K = \left(\frac{P_c}{P_0}\right)\left(\frac{T}{T_c}\right)^2$

and P_c = critical pressure of adsorbate (mm Hg)
P_0 = saturated vapor pressure of adsorbate (mm Hg)
T = adsorption temperature (K)
T_c = critical temperature of adsorbate (K)

Equation 2 has been proposed as a valid correlation for adsorption data at temperatures exceeding the critical temperature of the adsorbate.

3. DUBININ - ASTAKHOV (DA) METHOD

For a large number of microporous materials, the adsorption isotherm can be well characterized by the Dubinin - Radushkevich equation. However, for those microporous materials with heterogeneous distributions or strongly activated carbons, the Dubinin - Radushkevich equation fails to linearize the adsorption data[17].

$$W = W_0 \exp\left[-\left(\frac{-RT\ln P/P_0}{E}\right)^n\right] \tag{49}$$

The Dubinin - Astakhov equation,

where

W = weight adsorbed at P/P_0 and T
W_0 = total weight adsorbed
R = gas constant
T = Temperature (K)
E = characteristic energy
n = non-integer value (typically between 1 and 3)

is a generalized form of the Dubinin - Radushkevich equation (n=2) and has been found to fit adsorption data for heterogeneous micropores[18].

The Dubinin-Astakhov equation requires the parameters n and E to be calculated re-iteratively by non-linear curve fitting to the adsorption isotherm in the low relative pressure, micropore region. The values of n and E obtained are then used in equation 3.[19]

$$\frac{d\left(w/w_0\right)}{dr} = 3n\left(\frac{K}{E}\right)^n r^{-(3n+1)} \exp\left[-\left(\frac{K}{E}\right)^n r^{-3n}\right] \qquad (50)$$

where

r = pore radius
K =interaction constant = 2.96 kJ x nm^3 x mol^{-1} (N_2)
= 2.34 kJ x nm^3 x mol^{-1} (Ar)

A plot of $[d(w/w_0)]/dr$ versus r yields the DA Method pore size distribution (see Fig. II-8).

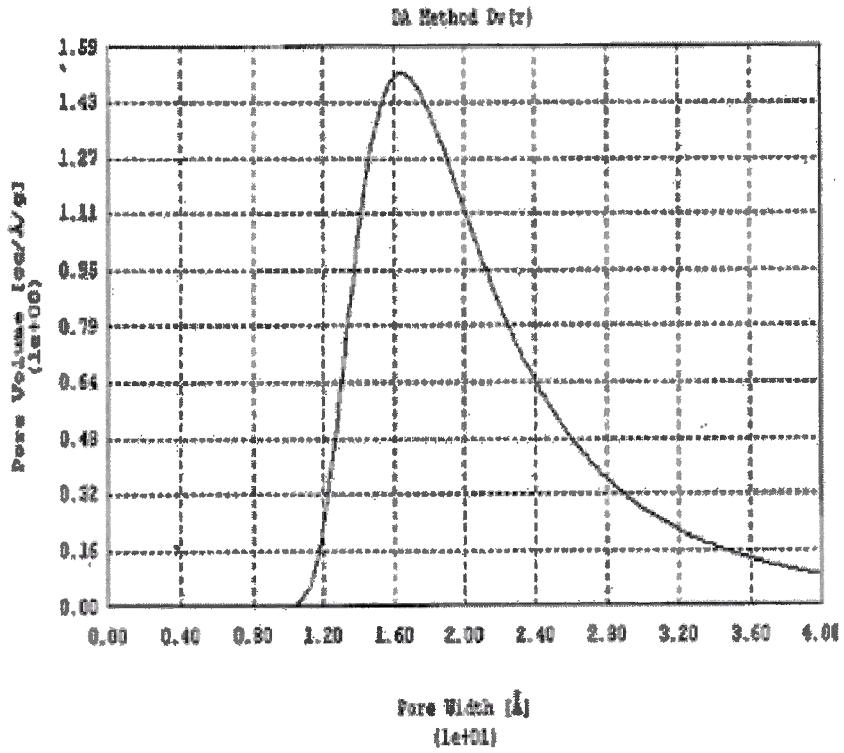

DA Method Dv(r)
1.59
1.43
1.27
1.11
0.95
0.79
0.64
0.48
0.32
0.16
0.00
Pore Volume [cc/Å/g]
(1e+00)
0.00
0.40
0.80
1.20
1.60
2.00
2.40
2.80
3.20
3.60
4.00
Pore Width [Å]
(1e+01)

FIGURE II-8

4. HORVATH-KAWAZOE (HK) METHOD

The HK method[20] enables the calculation of pore size distribution of micropores from the low relative pressure region of the adsorption isotherm. Many pore size distribution methods are derived from the Kelvin equation which describes the phenomenon of capillary condensation. Some have questioned the reliability of the capillary condensation approach in the small confines of micropores. The HK method is derived independently from the Kelvin equation.

$$RT \ln\left(\frac{P}{P_0}\right) = K\,\frac{N_S\,A_S + N_A\,A_A}{\sigma^4\,(\ell - d)}\ x \left[\frac{\sigma^4}{3\left(\ell - \frac{d}{2}\right)^3} - \frac{\sigma^{10}}{9\left(\ell - \frac{d}{2}\right)^9} - \frac{\sigma^4}{3\left(\frac{d}{2}\right)^3} + \frac{\sigma^{10}}{9\left(\frac{d}{2}\right)^9}\right] \qquad (51)$$

The HK method expresses the adsorption potential function within slit-like micropores as a function of the effective pore width:

where

K = Avogadro's number
N_S = number of atoms per unit area of adsorbent
N_A = number of molecules per unit area of adsorbate

$$A_S = \frac{6\,mc^2\,\alpha_s\,\alpha_A}{\frac{\alpha_s}{\chi_s} + \frac{\alpha_A}{\chi_A}} \qquad (52)$$

and m = mass of an electron
c = speed of light
α_s = polarizability of adsorbent
α_A = polarizability of adsorbate
χ_s = magnetic susceptibility of adsorbent
χ_A = magnetic susceptibility of adsorbate

$$A_A = \frac{3\,mc^2\,\alpha_A\,\chi_A}{2} \qquad (53)$$

$(\ell - d_s)$ = effective pore width
where $d = d_s + d_A$
and d_s = diameter of adsorbent molecule

d_A = diameter of adsorbate molecule
ℓ = distance between two layers of adsorbent
$\sigma = 0.858d/2$

By selecting effective pore widths in the micropore range, equation 45 can be used to calculate the corresponding relative pressures. From the adsorption isotherm, the amount of adsorption at each of these relative pressures is determined. Differentiation of weight (or volume) of gas adsorbed relative to the total uptake, W/W_0, with respect to the effective pore width yields a pore size distribution in the micropore range (See Fig. II-9).

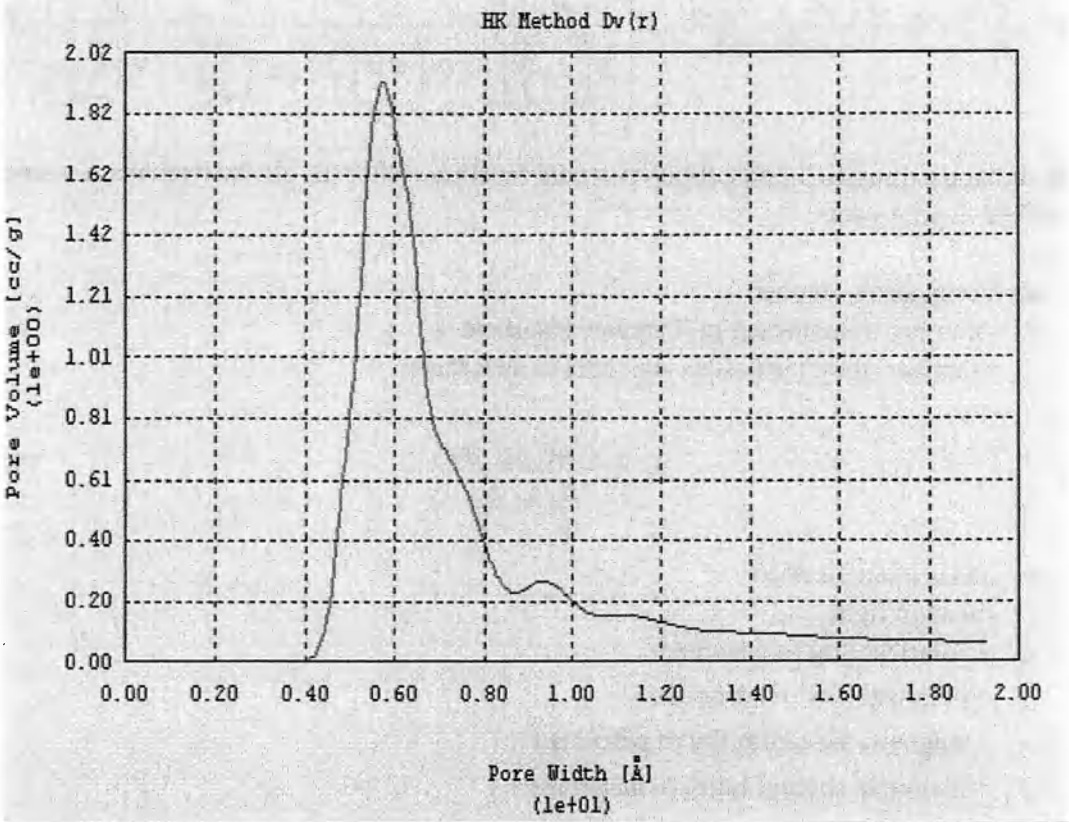


FIGURE II-9 HK Pore Size Distribution Plot.

5. SAITO-FOLEY (SF) METHOD

$$RT \ln \frac{P}{P_0} = \frac{3\pi K}{4} \times \frac{(N_S A_S + N_A A_A)}{(d/2)^4} \times \sum_{k=0}^{\infty} \left(\frac{1}{k+1} \right) G \tag{54}$$

Even though the HK method is adequate for materials with a predominance of slit-like pores (activated carbons, layered clays), certain solids (e.g., zeolites) are better represented assuming cylindrical pore geometry. Hence, the SF method[21] was developed as an alternative to the slit-like pore-based HK method. As with the HK method, the SF method enables the calculation of pore size distributions of microporous materials independently from the Kelvin Equation. The computational approach is analogous to that of the HK method, except that cylindrical pore geometry is assumed. Accordingly, equation (45) is replaced by

$$G = \left[1 - \left(\frac{d}{D} \right) \right]^{2k} \left[\left(\frac{21}{32} \right) a_k \left(\frac{d}{D} \right)^{10} - b_k \left(\frac{d}{D} \right)^{4} \right] \tag{55}$$

where

$$a_k = \left(\frac{-4.5 - k}{k} \right)^2 \tag{56}$$

and $a_0 = b_0 = 1$

$(D-d_s)$ = effective pore diameter

$$a_k = \left(\frac{-1.5 - k}{k} \right)^2 \tag{57}$$

with all other parameters having been defined in the previous section (HK method). The numerical solution of the above equations is again analogous to that of the HK method, and yields pore size distributions and cumulative pore volumes for cylindrical pores in the micropore range.

6. DENSITY FUNCTIONAL THEORY (DFT) METHOD

An alternative approach to interpret adsorption data on porous materials is by means of the Density Functional Theory (DFT).[22] This theory accounts for the fact that molecules adsorbed within pores tend to pack according to the strength of both surface forces and interactions with other molecules. That is, molecules adsorbed within small pores cannot pack as efficiently as those found within large pores. As a result, their molar density varies as a function of pore size. To take advantage of this variation, the experimental isotherm on a porous solid can be interpreted in terms of a Generalized Adsorption Isotherm (GAI) equation:

$$N\left(P/P_0\right)=\int_{W_{MIN}}^{W_{MAX}} N\left(P/P_0,W\right)x\,f(W)\,x\,dW \ \ldots \qquad (58)$$

where

$N(P/P_0)$ = experimental adsorption isotherm data
W = pore width (assuming slit-like pores)
$N(P/P_0,W)$ = isotherm on a single pore of width W
$f(W)$ = pore size distribution function

The GAI Equation simply states that the total isotherm is the sum of a number of individual "single-pore" isotherms multiplied by their relative distribution, f(W), over a range of pore sizes. The DFT Method derives sets of $N(P/P_o,W)$ isotherms using the local mean-field molar density approximation[23]. Hence, the pore size distribution function f(W) can be obtained by solving the GAI Equation numerically.

The DFT method has largely been applied to the characterization of microporous carbons via nitrogen adsorption at 77 K [20,24,25]. In order to optimize the solution of the GAI Equation, the sets of individual $N(P/P_o,W)$ isotherms derived for the nitrogen-carbon system using reported parameters[21] are stored as a kernel of the GAI. However, solving the GAI Equation presents well-known mathematical difficulties, because as an ill-posed problem it has no unique solution. Instead of assuming a pore size distribution function a priori,[20,21,22] in the present case the GAI Equation is solved via a fast non-negative least square algorithm. When a large number of experimental data points is available, this approach, which involves the use of a regularization parameter, yields satisfactory solutions of the GAI Equation within a wide pore size range.

7. THERMAL TRANSPIRATION

At the low pressures commonly employed for micropore characterization, the phenomenon of thermal transpiration[26] can result in significant pressure measurement errors if not compensated. Thermal transpiration results in a pressure gradient between the sample at temperature, T_1 and pressure, P_1 and the pressure transducer at temperature T_2 and pressure P_2 if the inner diameter of the tubing between the two part of the system is very small compared with the mean free path of the gas. The relationship between pressure and temperature can be expressed as follows for very low pressures:

$$P_1 = P_2 \; x \; \sqrt{T_1/T_2} \tag{59}$$

At higher pressures, the empirical model of Liang[27,28] can be employed to calculate thermal transpiration corrections for measured pressures.

$$\frac{P_2}{P_1} = \frac{\alpha \phi^2 x^2 + \beta \phi x + \sqrt{T_1/T_2}}{\alpha \phi^2 x^2 + \beta \phi x + 1} \tag{60}$$

where
$x = 0.133 P_2 d$
P_1, P_2 are in Pascal
d = diameter of connecting tube (m)

$$\left.\begin{array}{r} \alpha = 2.52 \\ \beta = 7.68\left[1 - \sqrt{T_2/T_1}\right] \end{array}\right\} \text{for helium}$$

Φ is the pressure shift factor that varies for gases relative to the value 1.00 for helium and can be calculated by

$$0.27 \, \log\phi = \log D + 9.59 \tag{61}$$

where D is the molecular diameter of the gas in meters.

H. FRACTAL DIMENSION METHODS

Surface characterization methods based on fractal geometry[29] describe the topography of real surfaces in terms of a "roughness exponent" known as fractal dimension, D. Ideal surfaces, being relatively smooth, can be modeled using simple geometric concepts (e.g., $6L^2$ for cubes, $4\pi R^2$ for spheres, etc.). For such surfaces D = 2, because the surface area is proportional to X^2, where X is some characteristic dimension of the adsorbent (e.g., X = L for squares, R for circles, etc.). In contrast, real surfaces are generally rough because of atom packing arrangements and defects, kinks and dislocations, and pores themselves, depending on the scale considered. Many real surfaces present surface irregularities that appear to be similar at different scales. These surfaces are referred to as fractal because their magnitude is proportional to X^D, where D is a fractional exponent that generally assumes values between D = 2 (for smooth surfaces) and D = 3 (for surfaces so rough that they essentially occupy all available volume). The fractal dimension D can thus be used to quantify the roughness of real surfaces in terms of a single parameter.

Among the various approaches proposed in the literature to evaluate D, two in particular have gained popularity because they make use of single gas sorption isotherms for their calculations. These are the Frenkel-Halsey-Hill (FHH) method[30] and the Neimark-Kiselev (NK) method[31]. Each is described in turn below.

1. FRENKEL-HALSEY-HILL (FHH) METHOD

$$\log \frac{P_0}{P} = \frac{B}{V^s} \tag{62}$$

By noting that in the multilayer adsorption region the influence of surface forces tends to be smoothed out, several independent authors derived an isotherm expression of the general form[8]

$$D = 3 \left(1 + s \right) \tag{63}$$

where B is a parameter related to adsorbate-adsorbent and adsorbate-adsorbate interactions, V is the amount of adsorbed material, and the exponent s is a constant characteristic of a given adsorbent. Equation (1) came to be known as the Frenkel-Halsey-Hill (or FHH) equation. Pfeifer et al.[30] postulated that the FHH exponent s is related to the fractal dimension D of the adsorbent through the expression

$$D = 3 + s \tag{64}$$

In deriving equation (1) surface tension effects were neglected. That is, the assumption was made that the surface tension of the adsorbate at a molecular scale does not differ appreciably from its bulk liquid value. If surface tension effects are accounted for[32], the relationship between D and s is given by

In either case, for fractal surfaces a plot of log V *vs.* log $\left(\log \left(\frac{P_0}{P} \right) \right)$ should yield a straight line with negative slope s within the multilayer region of the isotherm.

2. NEIMARK-KISELEV (NK) METHOD

Combining thermodynamic and fractal arguments, Neimark[31] reasoned that above the onset of capillary condensation fractal surfaces should conform to the following equation,

$$S_{lg} = K \left(a_c \right)^{2-D} \tag{65}$$

$$a_c = r_k = \frac{2\, \gamma\, V_m}{R\, T\, \ln\left(\frac{P_0}{P}\right)} \qquad \text{(cf. 16)}$$

where D is the surface fractal dimension, K is a constant, a_c is the mean radius of curvature of the adsorbate-vapor interface, given by the Kelvin equation,

$$S_{lg} = \frac{RT}{\gamma} \int_{n}^{n_{\max}} \ln\left(\frac{P_0}{P}\right) dn \qquad (66)$$

and S_{lg} is the adsorbate-vapor interface area, given by the Kiselev equation,
with R being the universal gas constant, T the adsorption temperature, γ the adsorbate surface tension, V_m the adsorbate molar volume, and n and n_{max} the amounts of gas adsorbed at a given P/P_0 and at saturation, respectively. In other words, the cumulative area S_{lg} was taken to be equivalent to the adsorbent area measurable with a yardstick of a size proportional to a_c at any given P/P_0. Accordingly, a plot of log [S_{lg}] versus log [a_c] should also yield a straight line within the multilayer region of the isotherm, from which the fractal dimension D can be readily calculated.

III. INSTALLATION

1. AC POWER DISTRIBUTION

Incoming AC power is controlled by 2 circuit breakers. The first is for the vacuum pumps and the second is for all electronics.

Voltage input to the instrument is 120/240/100V. The requirement for a given instrument is indicated at the serial number plate affixed to the rear of the AUTOSORB.

The internal operating voltage is 120V and is controlled and protected by the electronics circuit breaker.

A UPS (Uninterruptible Power Supply) is recommended.

2. UPS INSTALLATION

CAUTION: The UPS Output voltage must be the same as the instrument's input line voltage
Example:

Instrument Input line voltage	UPS Output Voltage
100 VAC	100 VAC
120 VAC	120 VAC.
230 VAC	230 VAC
240 VAC	240 VAC

Refer to the UPS manual for operating instructions for the UPS itself.

2.1 Switch ALL circuit breakers OFF.
2.2 Move rocker switch located on the back of the AUTOSORB to down position from MAINS to UPS.
2.3 Plug in UPS' output to the UPS socket located on the back of the AUTOSORB.
2.4 Turn on UPS and then turn both AUTOSORB breakers back on.

3. PUMP VOLTAGES

The pump(s) for the AUTOSORB come(s)either in a high voltage or a low voltage range. The high voltage can operate at 220V/240V. The low voltage pump can operate at 120V/100V. All pumps are 50/60 Hz. Check the label on the pump(s) for voltage requirement. The pump(s) has (have) the same voltage requirement as instrument's input line voltage indicated on the serial number plate.

4. DESCRIPTION OF PANEL COMPONENTS: AUTOSORB-6 & AUTOSORB-3 MODELS

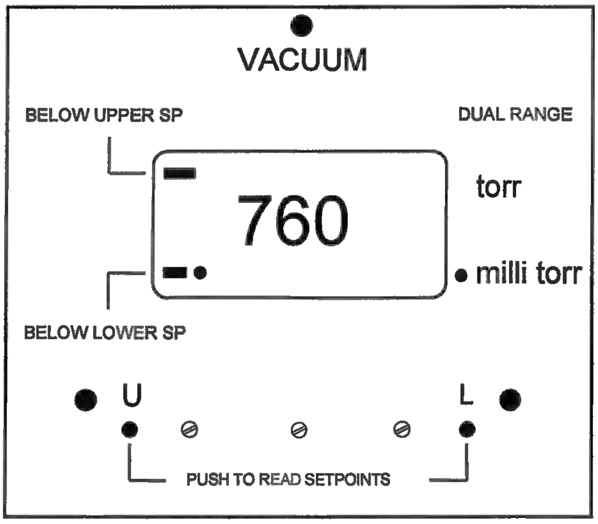
"METER" - The meter displays manifold temperature (°C), manifold pressure (mm Hg), sample station pressure (mm Hg), P_0 pressure (mm Hg) or outgassing temperature (°C) (AS- only). There may be zero offsets on the meter when displaying pressure readings; these offsets do not affect the operation of the AUTOSORB.

"PUSHBUTTON SELECT" - selects the reading to be displayed on the meter.

"VALVE STATUS" indicated by two-color LED's on the front panel which gives a complete plumbing schematic of the AUTOSORB. A green light indicates an open valve; a yellow light shows a closed valve.

"DEWAR FLASK STATUS" - indicated by columns of three LED's. The upper LED confirms the coolant level for the sample station - blue "ON" indicates level sensor (thermistor) contact with coolant. The center LED gives the direction of the Dewar flask - yellow "ON" indicates a down command. The bottom LED gives Dewar flask status - green "ON" indicating "good" status. The status is considered "good" if the drive is commanded down and the Dewar flask is down or the drive is commanded up and the Dewar flask is up with the level sensor in contact with the coolant. This LED is not illuminated when the Dewar drive is in motion.

"VACUUM GAUGE" - gives a display of low pressures. The gauge has two factory-set setpoints. The lower setpoint is set approximately at 10 millitorr. The upper setpoint is set at about 200 millitorr.



"CALIBRATION CHAMBER" - used for calibration of the manifold volume.

"ANALYSIS STATIONS" – Bulkhead fittings hold the sample cells during an analysis. The level sensor assembly connects immediately behind the sample cell fitting. The sample cell and level sensor assembly hang in parallel.

"P_0 CELL FITTINGS" - holds the P_0 cells during an analysis.

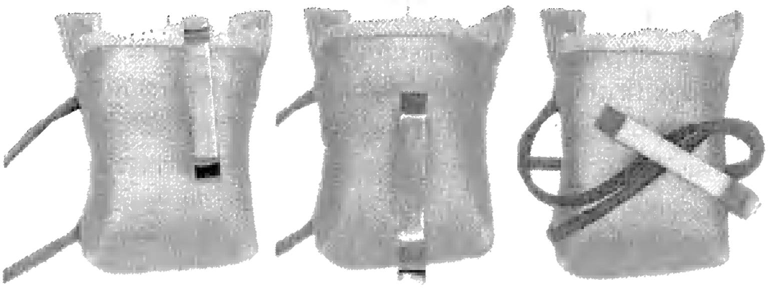
The following controls and fittings are found on the AUTOSORB-3 models only:

"MANTLE THERMOCOUPLE" "MANTLE POWER" and "TEMPERATURE SET" - located on the panel behind each of the three cell fittings on the outgassing stations.

"COLD TRAP" - Used to prevent diffusion of sample degassing products and oil vapor from the vacuum pump into the degassing manifold and contaminates from the degassing samples into the vacuum pump. The glass tube is inserted into the cold trap fitting in the same manner as the sample cells. The cold trap Dewar flask should be filled with liquid nitrogen and mounted on the panel by inserting its hook into the bracket provided.

A second VACUUM GAUGE is also built in to monitor the degassing manifold and samples.

Note: It is important to fasten heating mantle with a sample cell in a correct manner (see examples below).



INCORRECTLY SITUATED MANTLE CLAMP AND CELL

CORRECTLY SITUATED MANTLE CLAMP AND CELL

IV. OPERATION

A. INITIAL SETUP

The AUTOSORB requires a minimum amount of setup before powering the system on for the first time. The system requires the following:

Gas connections.
Tools required: 7/16" wrench (not supplied).
Connect adsorbate and helium gases to the lower back panel using the input lines supplied. It is recommended to use high purity helium and adsorbate gases (99.99% or higher). Attach a dual stage regulator with stainless steel diaphragm to the tank. Connect the regulator to the gas-input connector at the rear of the unit using the 1/8" copper tubing and nut & ferrule set supplied. It may be necessary to obtain an adapter in order to connect the tubing to the regulator. A suitable regulator assembly (P/N 01207) complete with shut-off valve, CGA580 cylinder fitting and 1/8" outlet fitting is available from Quantachrome. The regulator should be set to deliver 10 PSIG (70 kPa).

The AUTOSORB-6 requires a 1800 VA power line and the AUTOSORB-3 requires a 2400 VA line with the vacuum pumps supplied.

1. CONNECTING THE PC TO THE AUTOSORB

The minimum PC requirements are Windows 98, mouse, keyboard, 3.5" FDD, 8Mb of RAM, Pentium processor, color monitor, at least 5 Mb of available hard disk space, and a free RS232 serial port.

The proper cable and connectors are necessary to connect the PC to the AUTOSORB. The Autosorb is supplied with a 9-pin female to 25 pin male serial cable (p/n 26056).

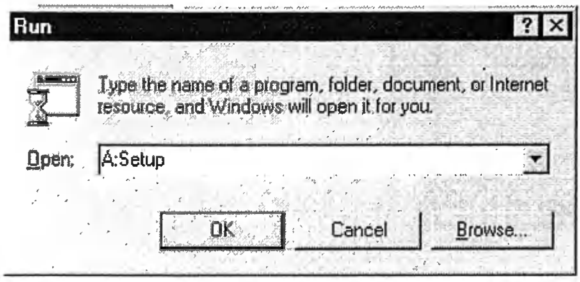
a. First, ensure that the PC is working properly.
b. Plug the male end of the serial cable into the 25 pin socket labeled "SERIAL PORT" at the rear of the AUTOSORB.
c. Plug the female end of the serial cable into the serial port of the PC.
d. Ensure the printer is properly connected to the computer.

2. INSTALLING THE SOFTWARE

IMPORTANT: Make backup copies of the Quantachrome® program disks and store them in a safe place.

Start Windows® if it is not already running.
Place Disk 1 in Drive A:

Select [RUN], type A:SETUP in the dialog box and click [OK].



Type the name of a program, folder, document, or Internet resource, and Windows will open it for you.

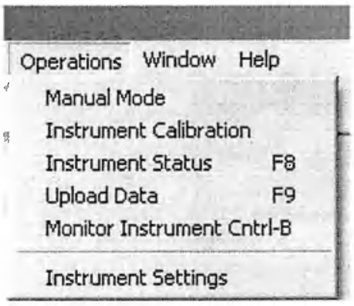
Open: A:Setup

Setup proceeds under the familiar InstallShield® Wizard.
Answer the questions regarding user information, default directories etc appropriately.
When asked to do so, insert Disks 2 and 3 and click on [CONTINUE].

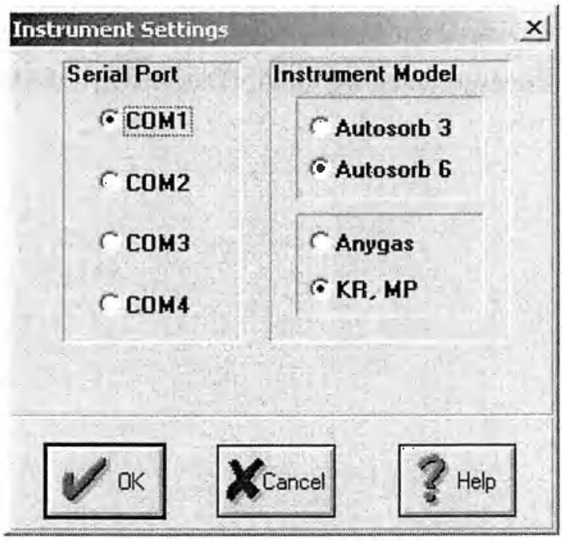
SETUP creates a new Windows group called QUANTACHROME CORPORATION.

B. STARTING THE PROGRAM

1. Double click on the QUANTACHROME CORPORATION windows group and then double click on the AS icon.
2. Select [OPERATIONS] from the menu bar and [INSTRUMENT SETTINGS] from the dropdown menu.



Use the instrument settings dialog box to verify that the model of the AUTOSORB and the serial port of the computer to which it is attached have been set correctly.


Instrument Settings

Serial Port
● COM1
○ COM2
○ COM3
○ COM4

Instrument Model
○ Autosorb 3
● Autosorb 6
○ Anygas
● KR, MP

When all the entries are correct, click [OK].

C. TURN-ON

To start the AUTOSORB, first turn on the vacuum pump, and then the electronics breaker on the lower back panel of the main system. The PC monitor will display several messages in the AUTOSORB Monitor window such as:

```
Quantachrome Corporation  Autosorb - 6B  Mk. 3.0
Instrument software version: 2.55
Compiled:  Sep 17 1999 15:57:22
22 bit A/D conversions enabled.
Magnalatch Valve Initialization...
Building Cell pressures to initialize valves. Please wait...
Magnalatch initialization complete.
Checking system vacuum status...
Waiting for vacuum to reach lower setpoint...
AnyGas Instrument.
Manifold volume: 32.061802 cc.
LEAK TEST MANIFOLD (Y/N) ? Y
MANIFOLD PASSED LEAK TEST (-0.015065 mm) - PRESS ANY KEY Starting Multitasker
```

These messages will vary according to instrument model/type.
After a short delay during which the system does some self tests the system will display the manifold volume that it has stored in its non-volatile memory. The system will offer the option of performing a leak test on the manifold. If the system has been off for more than an hour, a 15 minute warm-up should be allowed before answering this question. If selected, the leak test will take about 5 minutes.

Note: If the AUTOSORB cannot reach the lower vacuum set point, the leak test cannot be performed. If the <ENTER> key is pressed before the lower set point is reached the screen will display the message: CANNOT REACH VACUUM.

If, when restarting the AUTOSORB after a shut-down, the valve lights are not illuminated showing that the system is over-pressurized and will not initialize, remove the sample cell or stainless steel slug from one or more of the sample stations to allow the excess pressure to dissipate.

The instrument is now ready to analyze samples.

D. SHUTTING DOWN THE AUTOSORB

It is recommended that the AUTOSORB be left on at all times if it is to be used on a regular basis. However, if the instrument will not be used for a prolonged time, the following procedures should be used to shut it down.

1. SHORT TERM SHUT-DOWN

a. Insert sample cells or stainless steel dowels in the sample stations, P_0 stations and, on the AUTOSORB-3, each outgassing station.

b. Turn off the electronics and the vacuum pump(s).

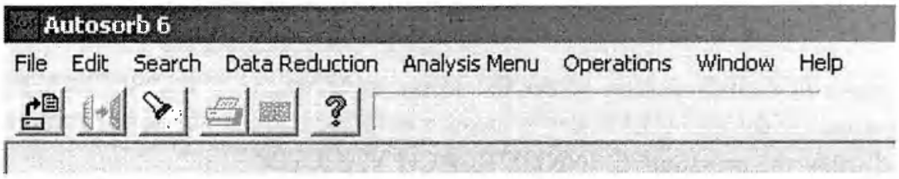
2. LONG TERM SHUT-DOWN

Follow steps a and b above. In addition, disconnect the gas input lines from the instrument.

NOTE: If, when restarting the AUTOSORB after a shut-down, the system shows over-pressurization and will not initialize, remove the sample cell or stainless steel dowel from one or more of the sample stations to allow the excess pressure to dissipate.

E. OPERATING THE AUTOSORB

When the program is loaded, a menu bar appears at the top of the window.



All the functions of the AUTOSORB (except degassing on an AUTOSORB-3) are accessible through this menu bar. Each of these choices has its own drop down menu.

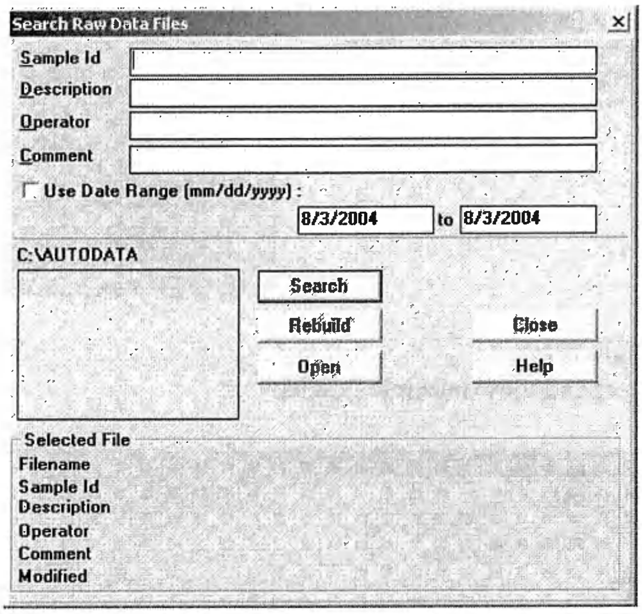
FILE and EDIT Menus

FILE and EDIT Menus have normal Windows® functions.

Note: File types that can be accessed in AUTOSORB Multistation software are:
- *.RAW - Raw data files containing P/Po and volume data
- *.DRF – Data raw data files containing P, Po and volume data
- *.RPT – Report files containing report data

SEARCH

Select [Search Raw Data Files] from the drop down menu. The default directory, as determined by the [SET DATA DIRECTORY] function, will be searched for the appropriate files.



☐ Use Date Range (mm/dd/yyyy): 8/3/2004 to 8/3/2004

C:\AUTODATA

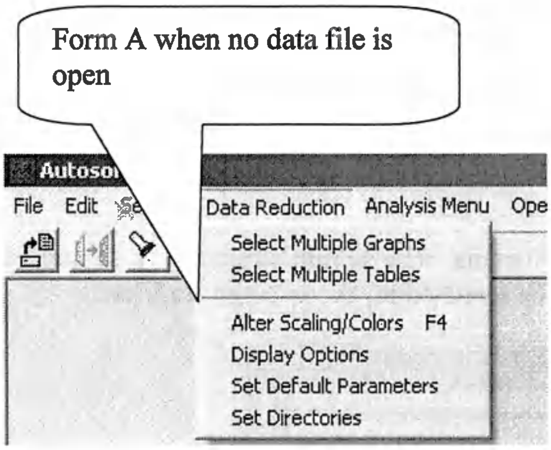
You can search for data files that match your search criteria. For example you can search for all data files where the Sample Description is 'GRAPHITE'.

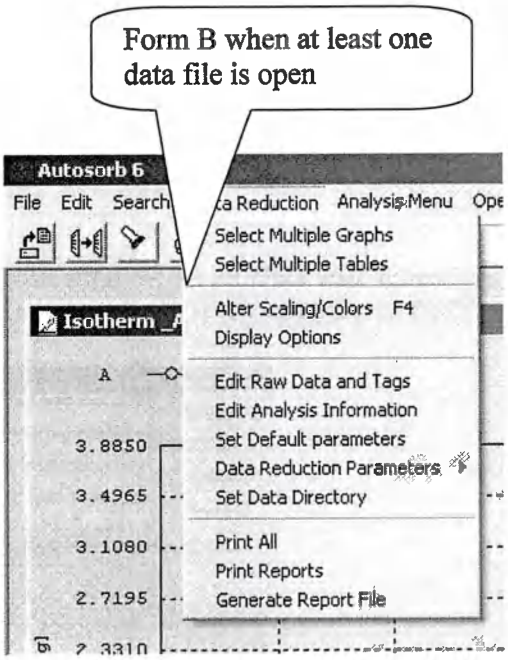
Enter a sample id, description, operator or comment. You can enter a combination of these to narrow your search. You can enter in lower or upper case. Leave all fields empty to display all files. Click on the Search button to start.

Click on the Rebuild button to rebuild the database if you think it is out of date. (The database is rebuilt whenever a new file is uploaded from the instrument.) The selected file's details will be displayed at the bottom of the dialog box.

DATA REDUCTION

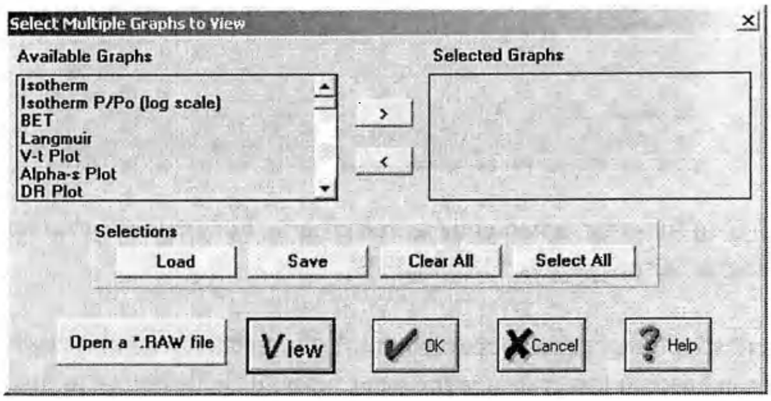
Data Reduction menu has two forms:


Form A when no data file is open


Form B when at least one data file is open

SELECT MULTIPLE GRAPHS

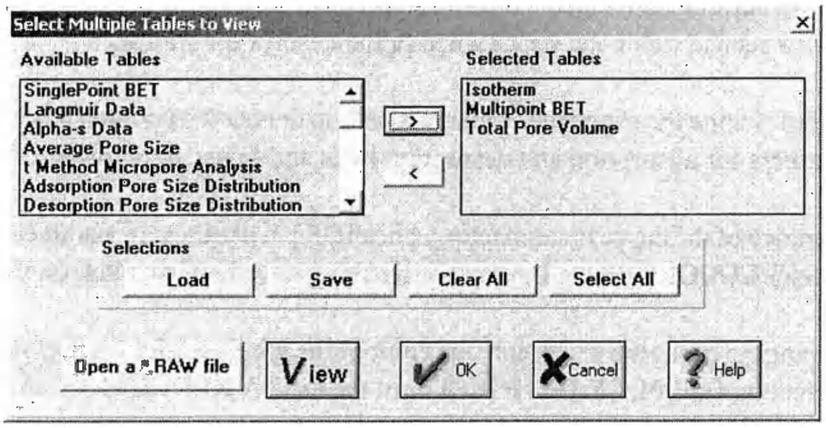
Use this function to select and view multiple graphs.



To add a graph to the list to be viewed, select it in the panel on the left and click the right arrow (>). After selecting the desired graphs, and if a data file was already open click on [VIEW] to generate the graphs and [OK] to return to the previous screen to see the graphs. Additionally, a new file can be loaded for viewing by clicking on [OPEN A *.RAW FILE]. This brings up the same dialog box as [OPEN] in the [FILE] drop down menu and allows additional files to be loaded. All the graphs can be selected or deselected by clicking on [SELECT ALL] or [CLEAR ALL]. To save the list for future use click on [SAVE] and give it a unique name (max 8 characters). To recall a saved list, click on [LOAD].

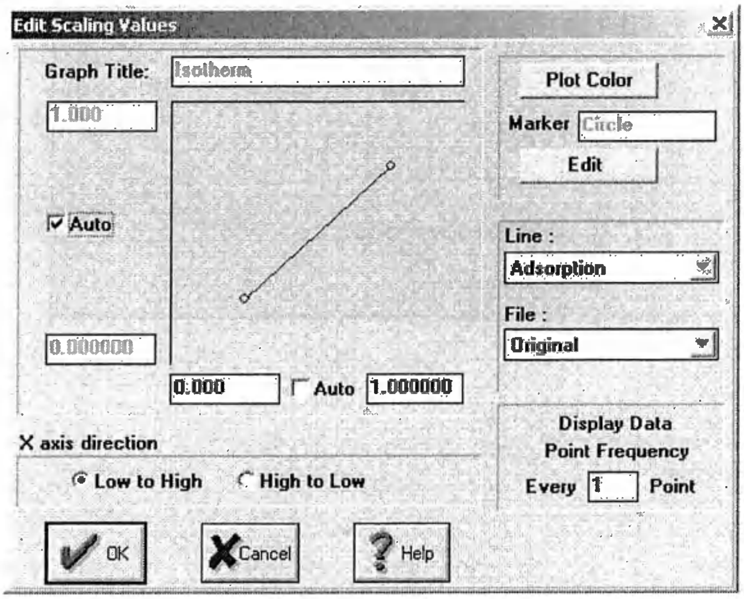
SELECT MULTIPLE TABLES

The SELECT MULTIPLE TABLES drop down menu is the same as the SELECT MULTIPLE GRAPHS drop down menu except that tabular data reports can be selected instead of graphs. All other functions are identical.



ALTER SCALING/COLORS

Use his dialog box to set the X- and Y- axes scales, the markers and the color of the curve (lines and pints) of each plot. For isotherms and other lines, different colors can be set for the adsorption and the desorption branches and best fit where appropriate.



Graph Title: Isotherm

1.000

☑ Auto

0.000000

0.000 ☐ Auto 1.000000

● Low to High ○ High to Low

Marker: Circle

Line: Adsorption

File: Original

Display Data Point Frequency

Every 1 Point

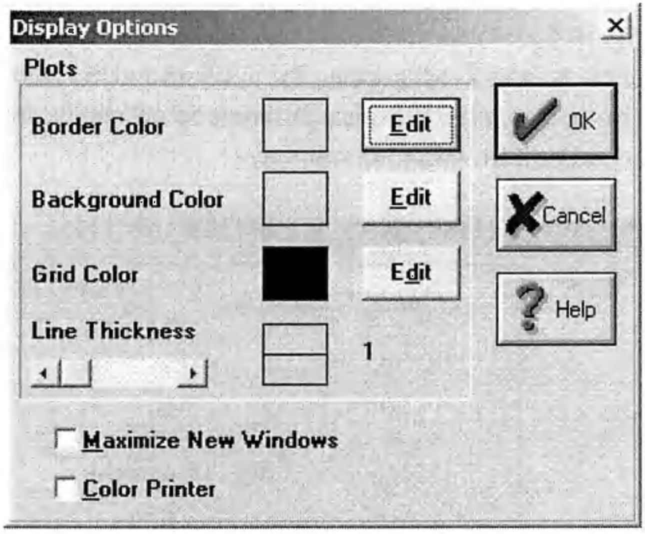
To change the graphing parameters, first select the graph to be altered from the drop down list (double click on it with the left mouse button). Each axis can be scaled manually or automatically. If manual scaling is desired, click the [AUTO] button off, then enter the desired maximum and minimum values in the X and Y axes scale boxes.

Click on [PLOT COLOR] to bring up a selection of 48 colors, each of which can be assigned to the line being edited. In addition, if desired, custom colors can be developed and assigned. For isotherms and other curves, a second color can be assigned to the desorption branch.

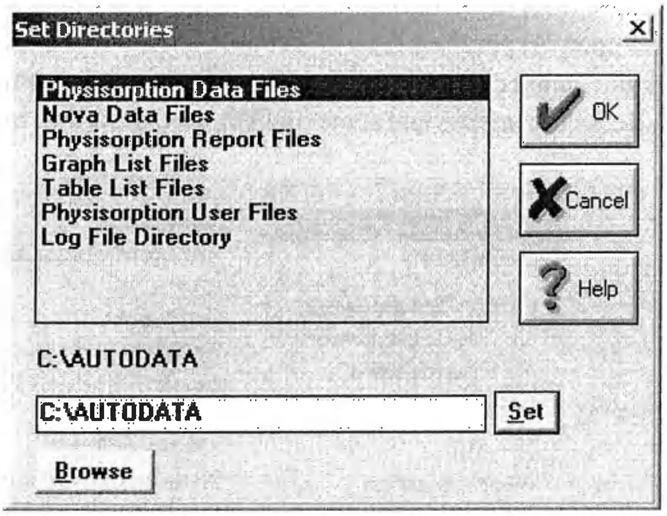
Click on [EDIT] to change the shape of the markers used to denote data points. It is recommended to use different markers for adsorption and desorption lines and to use dots for best fit lines.

When the appearance of the curve is satisfactory, click [OK] to use the new parameters. To close the ALTER SCALING/COLORS dialog box without making any changes, click on [CANCEL].

In addition to changing each line in a graph, the color of the graph border, background and grid can be altered by selecting [DISPLAY OPTIONS] from the DATA REDUCTION drop down menu.



SET DATA DIRECTORY


Set Directories

Physisorption Data Files
Nova Data Files
Physisorption Report Files
Graph List Files
Table List Files
Physisorption User Files
Log File Directory

C:\AUTODATA

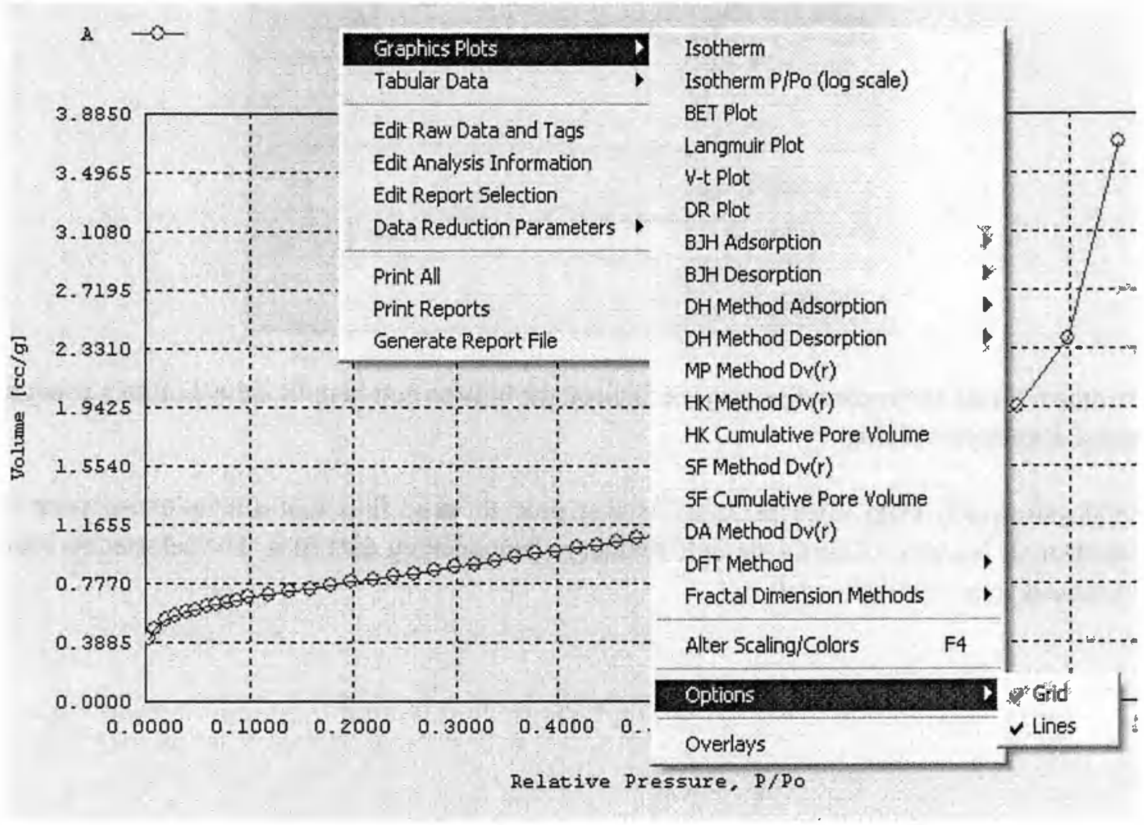
C:\AUTODATA

Enter the full path to the data directory, or click on the browse button to find the directory using the Browse Directories dialog.

The Physisorption Data Files directory is that used to store files that are uploaded from the instrument. It is also used as the default directory when opening data files. The selected directory will remain active until changed.

FLOATING MENU

Right mouse click on an open graph or table to reveal a detailed menu which gives access to all available graphs, tables and data reduction parameters, etc. Several items of this menu can also be accessed from the Data Reduction menus and some of them were described in the previous section.

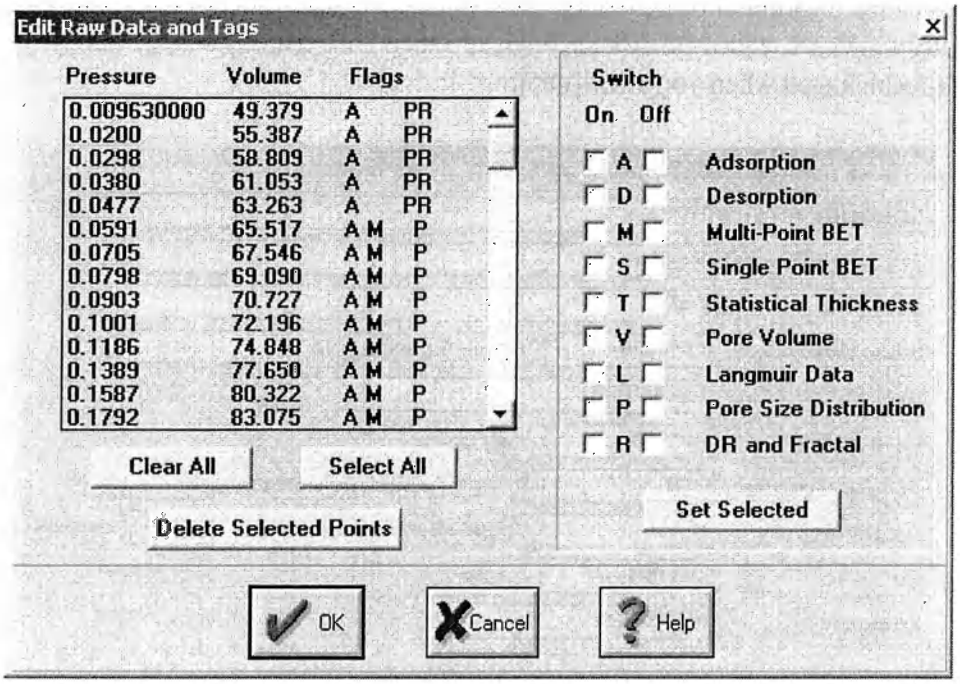


EDIT RAW DATA AND TAGS

Use this to designate which data points will be used in a particular calculation. Points can also be deleted. Use with caution! The tag(s) or flag(s) next to pressure and data values show for which calculation(s) a point will be used.

A	for inclusion in the adsorption isotherm.
D	for inclusion in the desorption isotherm.
M	for inclusion in the multipoint BET calculation.
S	for the single point BET calculation (limited to one point)
T	for inclusion in the statistical thickness calculations.
V	for inclusion in the pore volume calculation (limited to one point)
L	for inclusion in the Langmuir calculation.

P	for inclusion in the pore size distribution calculation.
R	for inclusion in the Dubinin - Radushkevich Dubinin Astakhov and Fractal calculations.



Pressure	Volume	Flags
0.009630000	49.379	A PR
0.0200	55.387	A PR
0.0298	58.809	A PR
0.0380	61.053	A PR
0.0477	63.263	A PR
0.0591	65.517	A M P
0.0705	67.546	A M P
0.0798	69.090	A M P
0.0903	70.727	A M P
0.1001	72.196	A M P
0.1186	74.848	A M P
0.1389	77.650	A M P
0.1587	80.322	A M P
0.1792	83.075	A M P

Switch

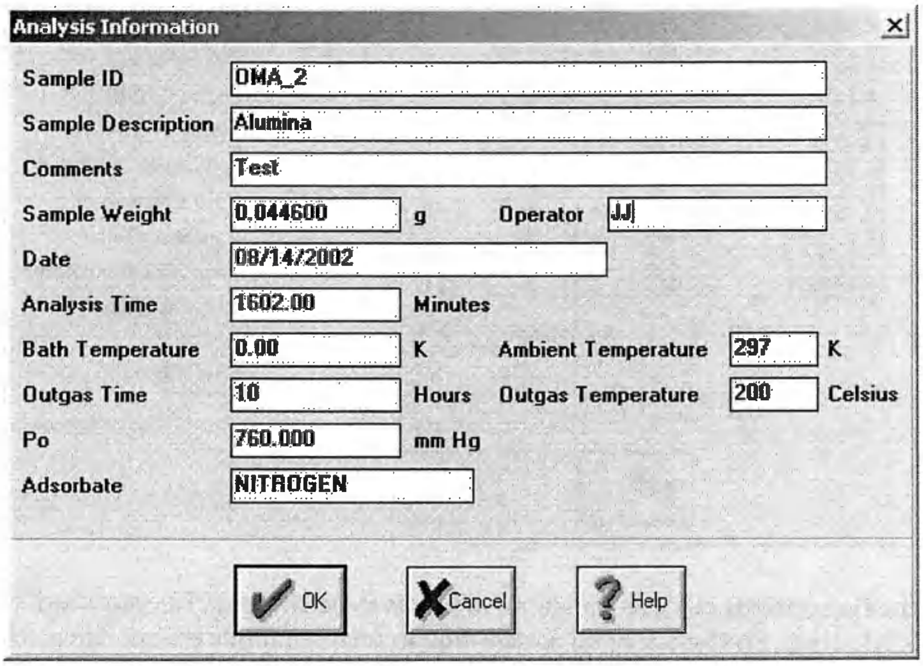
On		Off	
☐	A	☐	Adsorption
☐	D	☐	Desorption
☐	M	☐	Multi-Point BET
☐	S	☐	Single Point BET
☐	T	☐	Statistical Thickness
☐	V	☐	Pore Volume
☐	L	☐	Langmuir Data
☐	P	☐	Pore Size Distribution
☐	R	☐	DR and Fractal

To change the flag settings click on one or more points to be changed. Use standard Windows® functions CTRL-click, Shift-click or click-and-drag to select multiple points. Then select the desired flag settings for those highlighted points. A flag is added to a point when the ON box next to the function name is checked. A flag is removed from a point when the OFF box next to the function name is checked. When all flag switches have been made, click on [SET SELECTED].

To delete one or more data points, highlight them and then click on [DELETE SELECTED POINTS]. If a point is deleted by mistake, it can be recovered by closing the file without saving it, and then reloading it.

EDIT ANALYSIS INFORMATION

Use this to alter the information (text and data) that appears in the header of each page of the report. If a parameter which is used for calculating reduced data is changed, such as the sample weight, the data will be recalculated when you click [OK].



Sample ID	OMA_2				
Sample Description	Alumina				
Comments	Test				
Sample Weight	0.044600	g	Operator	JJ	
Date	08/14/2002				
Analysis Time	1602.00	Minutes			
Bath Temperature	0.00	K	Ambient Temperature	297	K
Outgas Time	10	Hours	Outgas Temperature	200	Celsius
Po	760.000	mm Hg			
Adsorbate	NITROGEN				

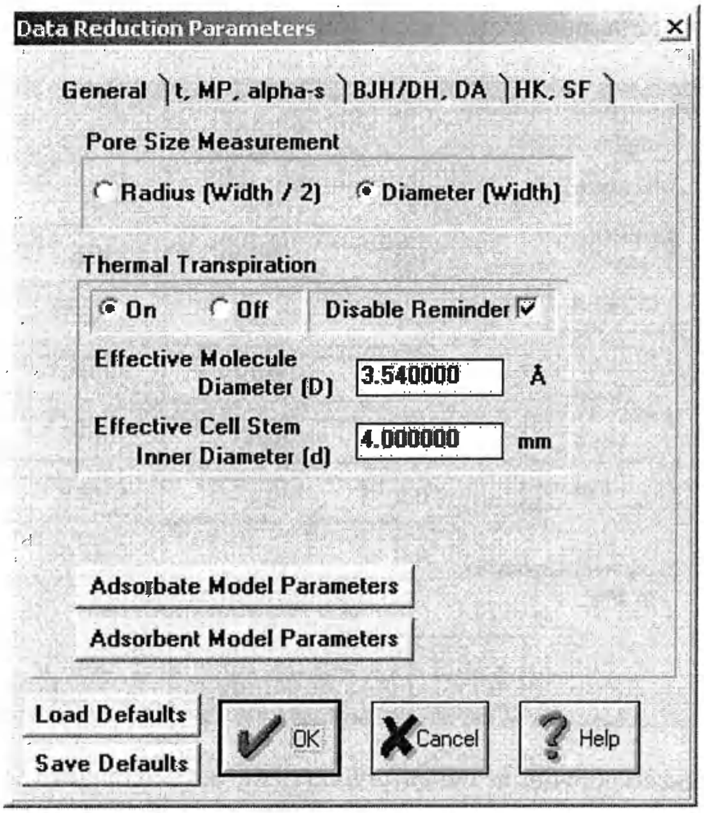
Any changes will be lost when the file is closed unless you save the file using [SAVE] or [SAVE AS] from the FILE drop-down menu.

EDIT REPORT SELECTION

The REPORT SELECTION dialog box is the same type as used in the SELECT MULTIPLE PLOTS and TABLES options. Use it to select the plots and tables that will comprise a report for a specific sample. Print a full report (both plots and tables) by clicking Print Reports in the Floating menu. Save a report to file (tables only) in ASCII format by clicking on Generate Report File in the Floating menu.

DATA REDUCTION PARAMETERS

This section is divided into three: General, Interpolation and DFT. The General Data Reduction Parameters Window displays the following information:



Pore Size Measurement

○ Radius (Width / 2) ● Diameter (Width)

Thermal Transpiration

● On ○ Off Disable Reminder ☑

Effective Molecule Diameter (D) 3.540000 Å

Effective Cell Stem Inner Diameter (d) 4.000000 mm

Thermal Transpiration is only important for very low pressures.

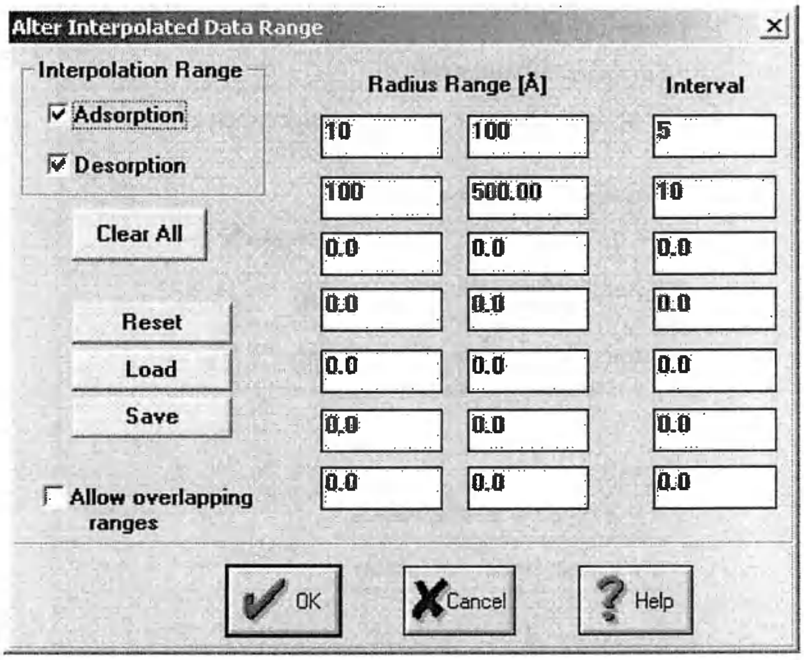
BJH and DH calculation can be smoothed by applying a moving average. Do not use too high moving average size. If needed, a value of 3 is recommended.

The various calculation models addressed here are discussed in detail in the Theory section.

Adsorbate model parameters should match the analysis gas. Adsorbent model parameters are critical only with DFT, HK, SF and DR.

INTERPOLATION

Use the ALTER INTERPOLATED DATA RANGE function to assign specific pore sizes for the BJH and DH pore size distribution calculations, rather than those calculated directly from experimental data points. The interpolated data are presented in a separate table (Floating menu>Tabular Data>Interpolation Pore Size Distribution). There is no corresponding plot.



Interpolation Range

☑ Adsorption

☑ Desorption

☐ Allow overlapping ranges

Radius Range [Å]		Interval
10	100	5
100	500.00	10
0.0	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0

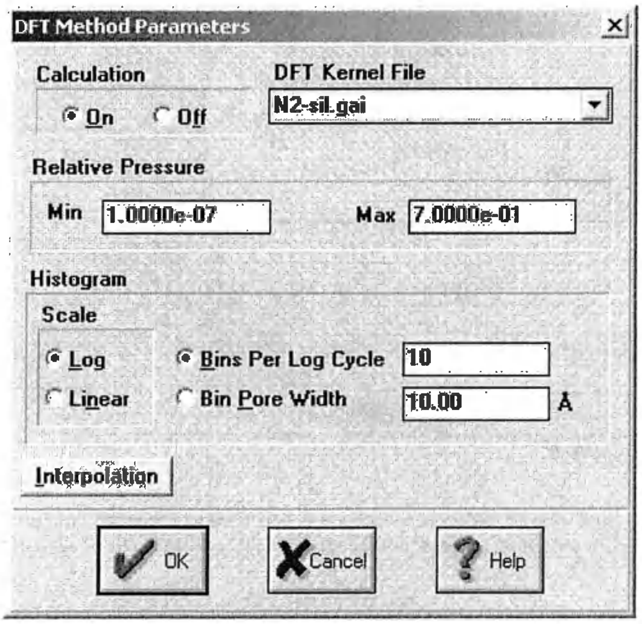
The values in left-hand column define the lower limit of the desired range over which interpolations are to be made. The values in the center define the upper limit of the desired range. The values in right-hand column (INTERVAL) set to the size of the increments between the two limits. For example, the first row will interpolate values from 10 to 100 Angstroms in 5 Angstrom increments.

[CLEAR ALL] sets all values in all ranges to zero.

If the [ALLOW OVERLAPING RANGES] box is checked, the ranges selected will be evaluated separately even if they include the same pore sizes but cumulative data will not be calculated. If it is not checked, pore sizes reported in a previous range will not be included in the report but cumulative data columns, as well incremental data will be displayed.

DFT METHOD

Use DFT METHOD PARAMETERS to set the parameters for Density Functional Theory and Monte Carlo calculations. Please see the Theory section to determine the appropriate settings. Bins per log cycle is a value that determines how many bins (or bars) there are for each log cycle in the histogram plot. The default value is 10; the minimum value is 1and the maximum value is 500.



Calculation: ● On ○ Off

DFT Kernel File: N2-sil.gai

Relative Pressure: Min 1.0000e-07 Max 7.0000e-01

Histogram

Scale: ● Log ○ Linear

● Bins Per Log Cycle 10

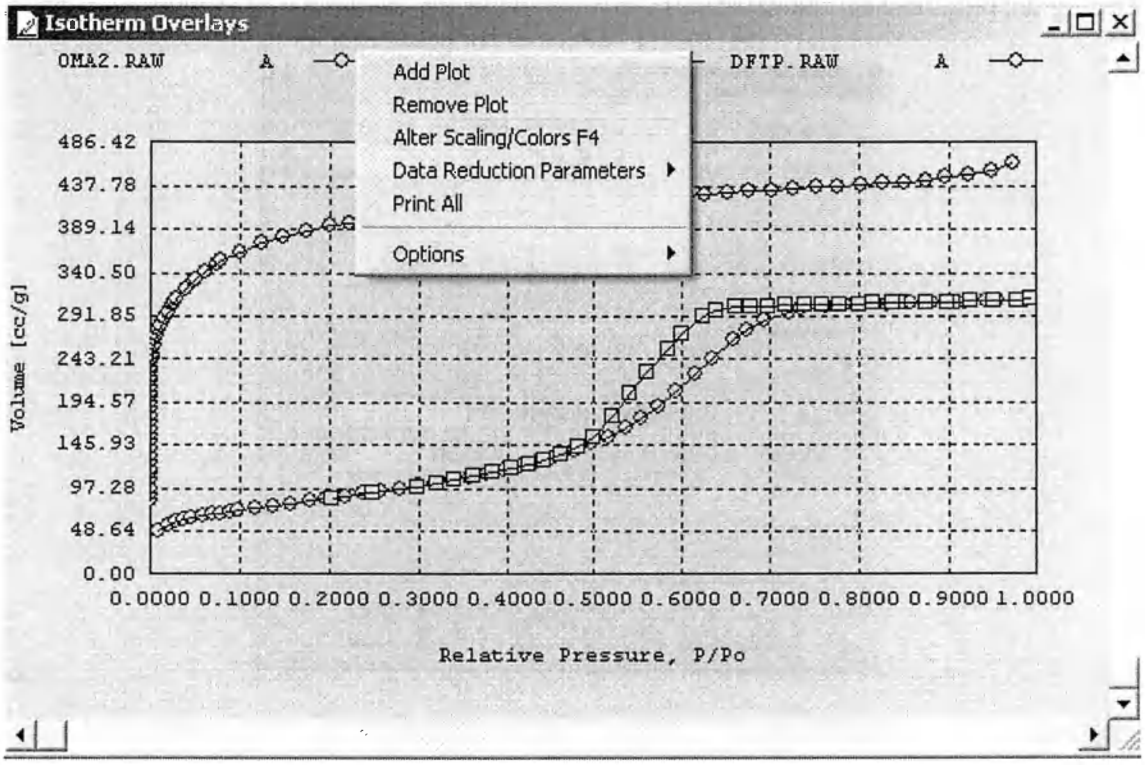
○ Bin Pore Width 10.00 Å

OPTIONS

Use this to turn on/off grid lines, lines connecting the data points and if appropriate, a best fit line. A function is turned on if a check mark appears next to its name.

OVERLAYS

Use this function to overlay data from two or more files. This function is available for all graph types except DFT. An overlay graph has its own abbreviated floating menu (see figure below).



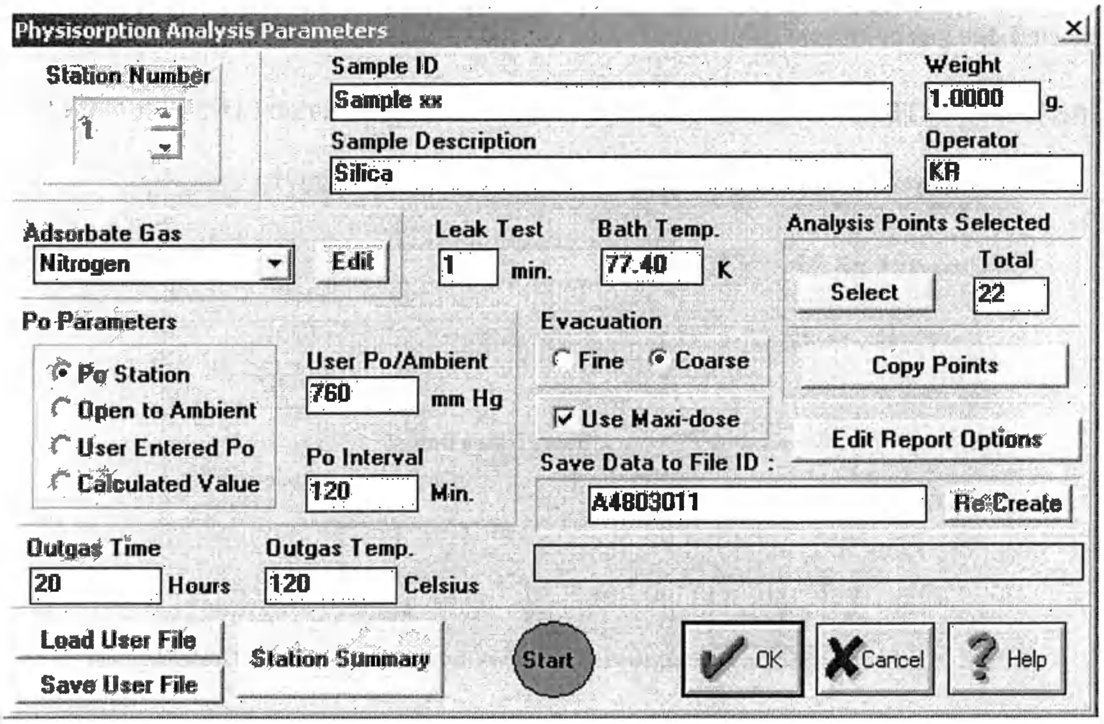
ZOOM

While viewing any graph on screen, you can select a portion of the graph to zoom in on. Place the cursor at the corner of the enlarged area to be viewed, press and hold the left mouse button and drag the cursor to the corner diagonally opposite to the starting corner. A drag box will be created enclosing the desired area. Release the mouse button to enlarge enclosed area to the full size of the graph. The display also contains a window in the main menu bar which shows the X- & Y-coordinates of the cursor position to aid in selecting the desired zoom area.

To restore the graph to its original full size, click [UNZOOM] from the floating menu.

PHYSISORPTION ANALYSIS PARAMETERS

This dialog box defines all the operational parameters that are used to analyze a sample.



Station Number: 1
Sample ID: Sample xx
Weight: 1.0000 g.
Sample Description: Silica
Operator: KR
Adsorbate Gas: Nitrogen
Leak Test: 1 min.
Bath Temp.: 77.40 K
Analysis Points Selected – Total: 22
Po Parameters: ● Po Station ○ Open to Ambient ○ User Entered Po ○ Calculated Value
User Po/Ambient: 760 mm Hg
Po Interval: 120 Min.
Evacuation: ○ Fine ● Coarse
☑ Use Maxi-dose
Save Data to File ID : A4803011
Outgas Time: 20 Hours
Outgas Temp.: 120 Celsius

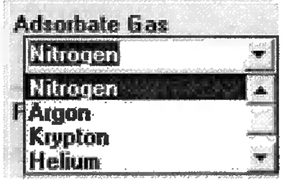
STATION NUMBER - Click on the up or down arrow until the desired station number is displayed in the window. As each station number is displayed, the sample analysis parameters set for that station will also be displayed throughout the dialog box.

SAMPLE ID - Enter a sample identification of up to 50 characters.

WEIGHT - Enter the sample weight (in grams) or leave the default weight of 1.0000 gram (the weight may be altered later during data reduction).

SAMPLE DESCRIPTION - Any brief description of up to 50 characters.

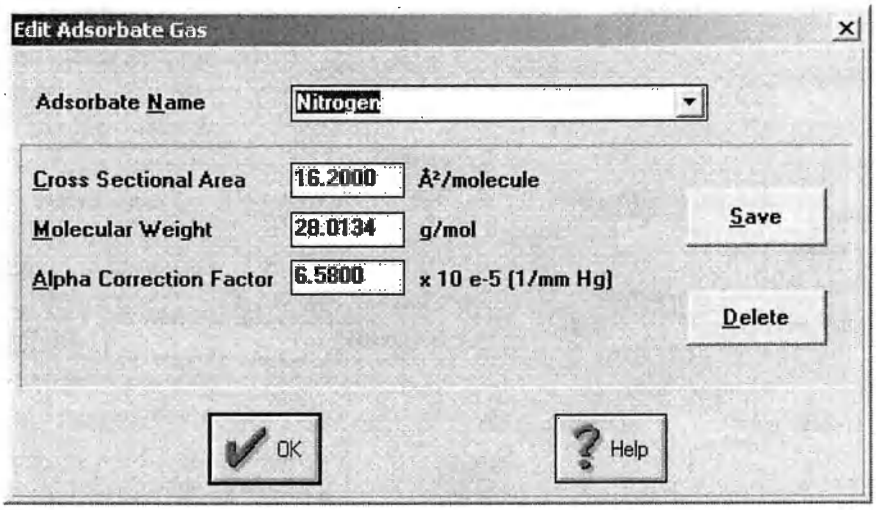
ADSORBATE GAS - Click on the down arrow ▼ to bring up a list of pre-programmed adsorbates.



Adsorbate Gas: Nitrogen

When selected, the gas name and its parameters are loaded.

EDIT GAS PARAMETERS - Use this dialog box to edit an existing gas or add a new one to the list.



Edit Adsorbate Gas

Adsorbate Name: Nitrogen

Cross Sectional Area: 16.2000 Å²/molecule

Molecular Weight: 28.0134 g/mol

Alpha Correction Factor: 6.5800 x 10 e-5 (1/mm Hg)

To edit an existing gas, first select it from the list.
Alpha Correction Factor is used to correct for non ideal gas behavior. For commonly used Alpha Correction Factors and Cross Sectional Areas see Table 1 Appendix 3. When all the parameters are acceptable, click on [SAVE].

To delete a gas from the list, select it from the list and click on [DELETE]. CAUTION If a USER file has been defined with a gas that has been deleted, an error message will appear when that file is called for initialization! USE WITH CAUTION.

To add a new gas to the gas table, select any gas and type over its name with that of the new gas. Enter new values for Cross Sectional Area, Molecular Weight and Alpha Correction Factor. Table 1 Appendix 3contains these values for the most commonly used gases. When all the parameters are acceptable, click on [SAVE].

P_0 PARAMETERS - The saturated vapor pressure of the adsorbate (P_0) is required for data acquisition and reduction in the AUTOSORB. The P_0 menu presents the following options for P_0 values. Only one option can be selected at any time.

● P_0 Station
○ Open to Ambient
○ User Entered P_0
○ Calculated Value

If *P_0 Station* is selected, place an empty P_0 cell in the P_0 station. During sample initialization the system will liquefy adsorbate in the P_0 cell and read the vapor pressure as needed during the analysis. If this option is selected the user should enter an approximate P_0 value in the User P_0/Ambient field. This value is used by the instrument in the initialization procedure.

If *Open to Ambient* is selected, the system will measure ambient pressure and use this value to calculate P_0 by adding 5 mm Hg for nitrogen or using the Clausius-Clapeyron Equation for krypton type gases (see appendix 5). When this option is chosen a cell or plug must be placed in the P_0 station. The system will perform a transducer scaling, then indicate that the cell or plug is to be removed.

User Entered P_0 means just that the value for P_0, in mm Hg, must be entered in the User P_0/Ambient field.

The *Calculated Value* method of determining P_0 is the same as Open to Ambient except that the AUTOSORB uses an operator entered value instead of measuring ambient pressure. If this method is selected, the operator must enter a value in mm Hg for ambient pressure in the User P_0/Ambient field.

USER P_0 /AMBIENT - This value will be used when P_0 Station, User Entered P_0 or Calculated Value is selected in the P_0 parameters field.

P_0 INTERVAL - The P_0 value is updated at a user selected interval when P_0 station is selected. The update time is the same for all active stations and can range from ten minutes to 999 minutes. Since the manifold and its transducer are required for the update, frequent updates can delay the acquisition of data points. An interval of 120 minutes is recommended for most analyses.

EVACUATION - Select "fine" to evacuate slowly if the sample is a fine powder that might elutriate if the system is evacuated rapidly. Select "coarse" to evacuate quickly when running pellets or heavy granular samples.

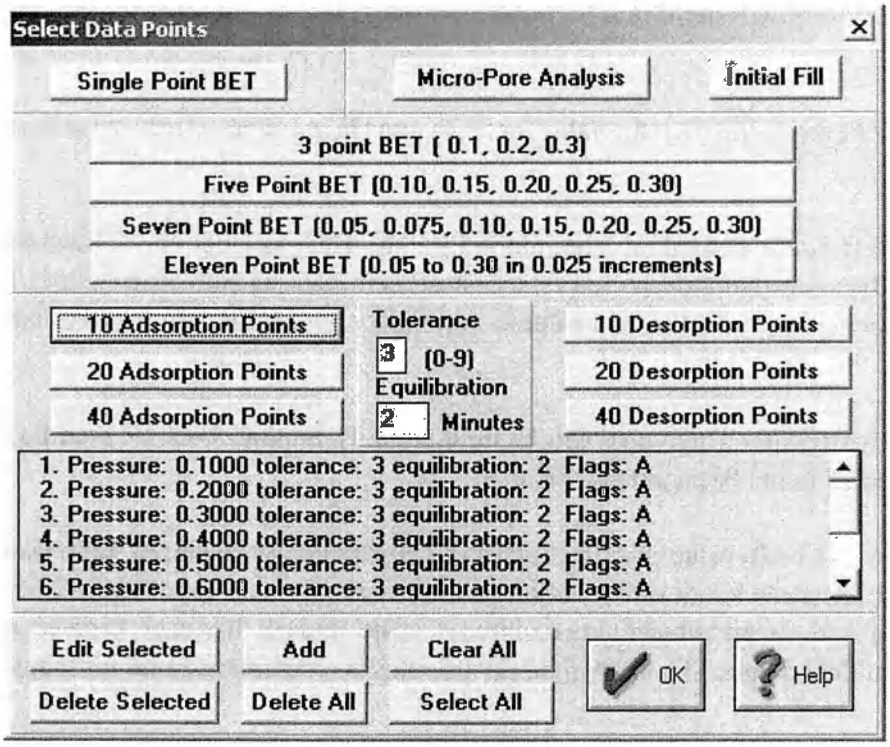
USE MAXI-DOSE - If you select this option an intelligent dosing algorithm is implemented. If the pressure falls below the allowed pressure tolerance, the algorithm will automatically increase the size of the dose. In this manner successively greater doses of gas are admitted into the sample cell, resulting in fewer doses and more rapid analysis times. In order to avoid overshooting, target pressures are decreased as the sample approaches equilibrium.

NOTE: MAXIDOSE is not to be used for MICROPORE MEASUREMENTS.

LEAK TEST - Specify the duration of the leak or outgassing test (from 0 to 30 minutes). Normal value is 1.

BATH TEMP - The temperature of the coolant bath (in kelvin) must be entered. If liquid nitrogen is used, the default value of 77.35 K may be left in.

ANALYSIS POINTS SELECTED - Click on [SELECT] to chose data points (P/P_0 values) you want to have measured.



Tolerance 3 [0-9]
Equilibration 2 Minutes

```
1. Pressure: 0.1000 tolerance: 3 equilibration: 2  Flags: A
2. Pressure: 0.2000 tolerance: 3 equilibration: 2  Flags: A
3. Pressure: 0.3000 tolerance: 3 equilibration: 2  Flags: A
4. Pressure: 0.4000 tolerance: 3 equilibration: 2  Flags: A
5. Pressure: 0.5000 tolerance: 3 equilibration: 2  Flags: A
6. Pressure: 0.6000 tolerance: 3 equilibration: 2  Flags: A
```

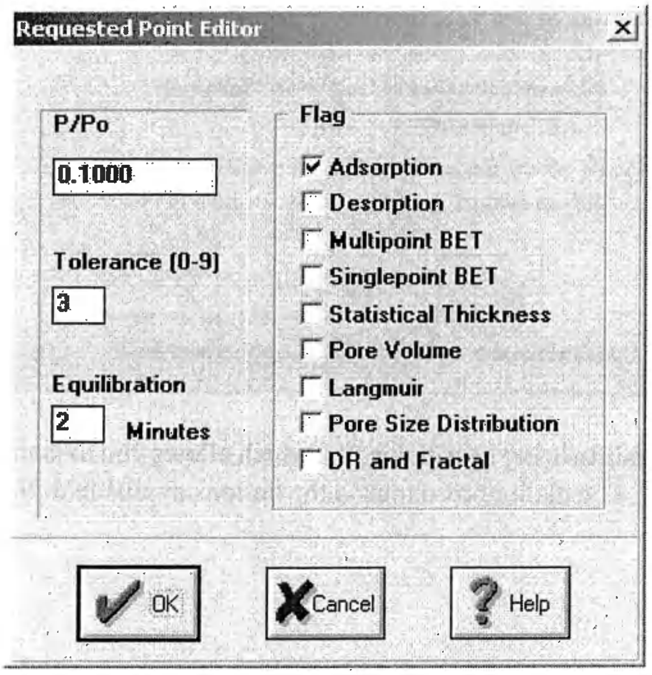
Before selecting any data points set "Tolerance" and "Equilibration". Each group of points selected will use the values displayed in the windows. Individual data points can be edited by double clicking on the point to be changed.

TOLERANCE - Select value from 0 to 9. A tolerance value of 0 (recommended for most applications) insures the tightest match between the P/P$_0$ values selected and those achieved (typically .001 atm.) while a tolerance of 9 results in a faster analysis with a looser relative pressure tolerance (typically .01 atm.). See Appendix 2 for further details.

EQUILIBRATION Select an equilibration time between 1 minute and 99 minutes. A value of 2 or 3 minutes is ideal in most cases. See Appendix 2 for further details.

NOTE: For MICROPORE MEASUREMENTS it is recommended to use Tolerance 0 and Equilibration time 4 minutes or more.

A number of preprogrammed points can be quickly added to the points list by clicking on the button(s) which most closely match your requirements. BET buttons automatically flag the points for BET calculation.
The values of any points in the list can be edited after selecting them.
Individual points can be added to the list; the list will automatically re-order to ensure points are presented in increasing P/P$_0$ for adsorption points followed by decreasing P/P$_0$ for desorption points.



P/Po: 0.1000

Tolerance (0-9): 3

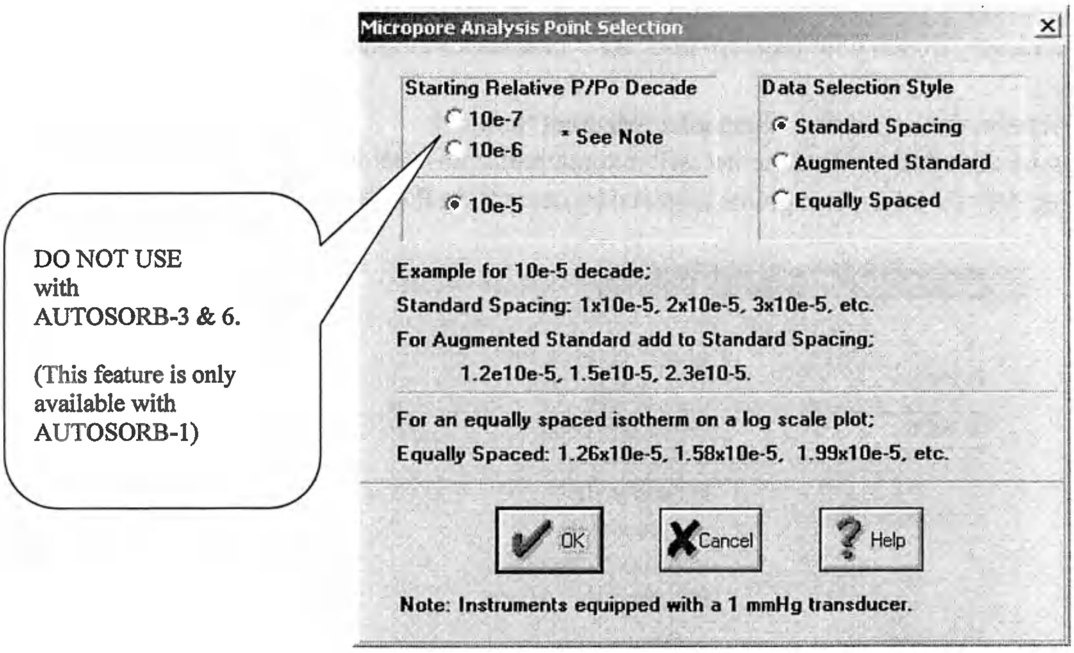
Equilibration: 2 Minutes

Flag
- ☑ Adsorption
- ☐ Desorption
- ☐ Multipoint BET
- ☐ Singlepoint BET
- ☐ Statistical Thickness
- ☐ Pore Volume
- ☐ Langmuir
- ☐ Pore Size Distribution
- ☐ DR and Fractal

A	appears if the point specified is from the adsorption branch of the isotherm.
D	appears if the point specified is from the desorption branch of the isotherm.
M	appears if the point is specified for use in the multipoint BET calculation.

S	appears if the point is specified for use in the single point BET calculation.
T	appears if the point is specified for use in the statistical thickness calculation for microporosity.
V	appears if the point is specified for use in the total pore volume calculation.
L	appears if the point is specified for use in the Langmuir calculations.
P	appears if the point is specified for use in the pore size distribution calculations (BJH and DH).
R	appears if the point is specified for inclusion in the Dubinin – Radushkevich, DA and Fractal calculations.

MICROPORE ANALYSIS POINT SELECTION



Micropore Analysis Point Selection

Starting Relative P/Po Decade
○ 10e-7
○ 10e-6
* See Note
● 10e-5

Data Selection Style
● Standard Spacing
○ Augmented Standard
○ Equally Spaced

Example for 10e-5 decade:
Standard Spacing: 1x10e-5, 2x10e-5, 3x10e-5, etc.
For Augmented Standard add to Standard Spacing:
1.2e10e-5, 1.5e10-5, 2.3e10-5.

For an equally spaced isotherm on a log scale plot:
Equally Spaced: 1.26x10e-5, 1.58x10e-5, 1.99x10e-5, etc.

Note: Instruments equipped with a 1 mmHg transducer.

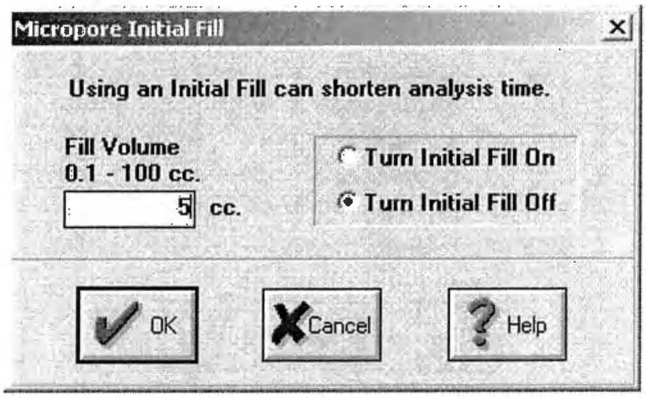
DO NOT USE
with
AUTOSORB-3 & 6.

(This feature is only
available with
AUTOSORB-1)

Click Micropore Analysis to bring up a dialog box which allows you to load a set of low P/P0 points for micropore analysis. The dialog box explains the options available to the operator.

INITIAL FILL can be used to reduce the time taken to fill micropores by pre-loading a volume of adsorbate to initially overcome the extended time it takes to add enough adsorbate to reach the desired first target relative pressure.

NOTE: INITIAL FILL is not recommended if you need detailed micropore size distribution.


Micropore Initial Fill

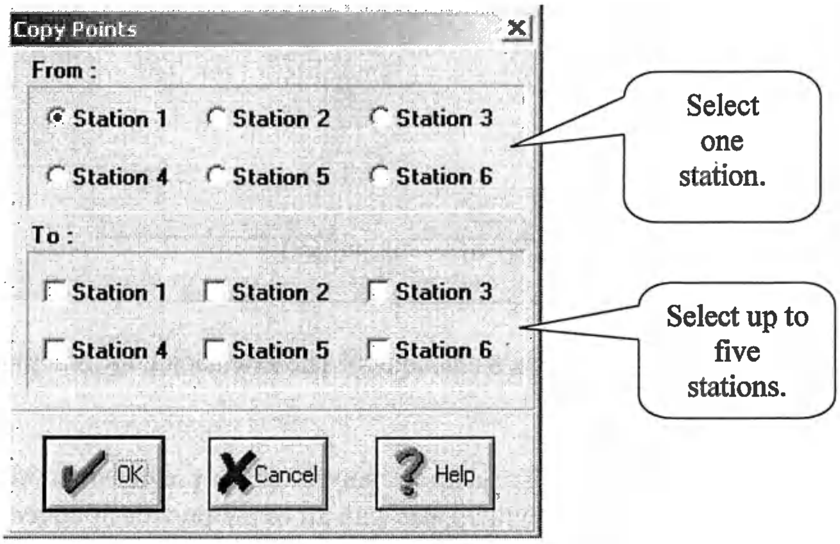
Using an Initial Fill can shorten analysis time.

Fill Volume
0.1 - 100 cc.
5 cc.

○ Turn Initial Fill On
● Turn Initial Fill Off

NOTE:The Micropore Adsorption points are available only if the Micropore Option has been installed.

COPY POINTS - Click on COPY POINTS in the Analysis Parameters screen to copy the data points, and their parameters, from any one station to one or more other stations. This eliminates the need to define the same set of points for each station doing the same analysis.


Copy Points

From :
● Station 1 ○ Station 2 ○ Station 3
○ Station 4 ○ Station 5 ○ Station 6

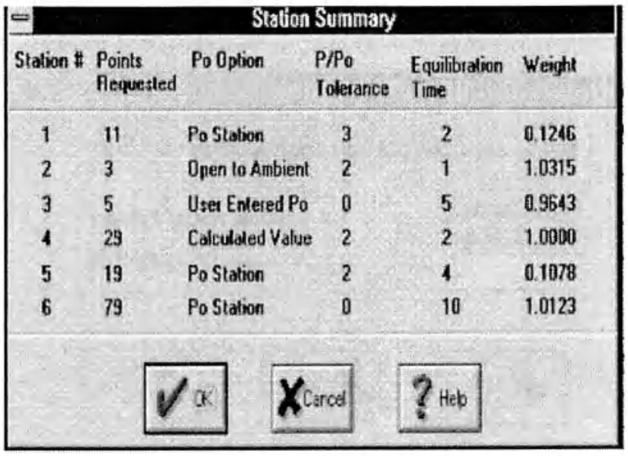
To :
☐ Station 1 ☐ Station 2 ☐ Station 3
☐ Station 4 ☐ Station 5 ☐ Station 6

Select one station.

Select up to five stations.

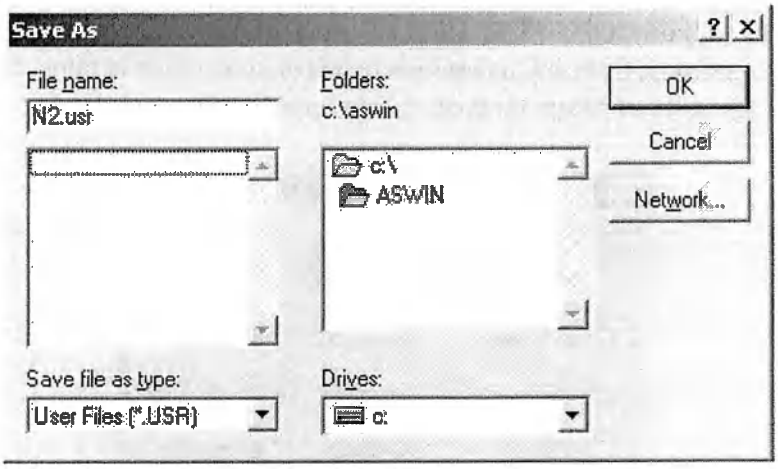
STATION SUMMARY - Click on STATION SUMMARY to review the number of requested points, P_0 option, P/P_0 tolerance, equilibration time in minutes, and sample weight for each station.

Note: The P/P0 tolerance and the equilibration time is the value for the first point for each station


Station Summary

Station #	Points Requested	Po Option	P/Po Tolerance	Equilibration Time	Weight
1	11	Po Station	3	2	0.1246
2	3	Open to Ambient	2	1	1.0315
3	5	User Entered Po	0	5	0.9643
4	29	Calculated Value	2	2	1.0000
5	19	Po Station	2	4	0.1078
6	79	Po Station	0	10	1.0123

SAVE USER FILE - To save the analysis parameters in a User file for use at a later time, click [Save User File].


Save As

File name: N2.usr

Folders: c:\aswin

Save file as type: User Files (*.USR)

Drives: c:

Enter a name of the file (max 8 characters). The extension USR is automatically added to the name of the file.

RETRIEVE USER FILE - To set up an analysis using a previously saved User File, click [Load User File]. Sample parameters will appear with all of the previously saved information filled in. This information may be edited as described above or accepted without change.

SAVE DATA TO FILE ID: - A default file name is assigned by the program having the following format: ASYMDDNN

AS -- represents AUTOSORB (The S will be replaced by the station number when the file is saved).

Y -- represents the year. Eg 4 represents 2004. File names reappear every 10 year cycle.

M -- represents the month. 1-9 represents the first nine months, A-C represent months 10-12.

DD -- represents the day of the month.

NN -- represents the sequential analysis of the day to be started. This number is automatically incremented.

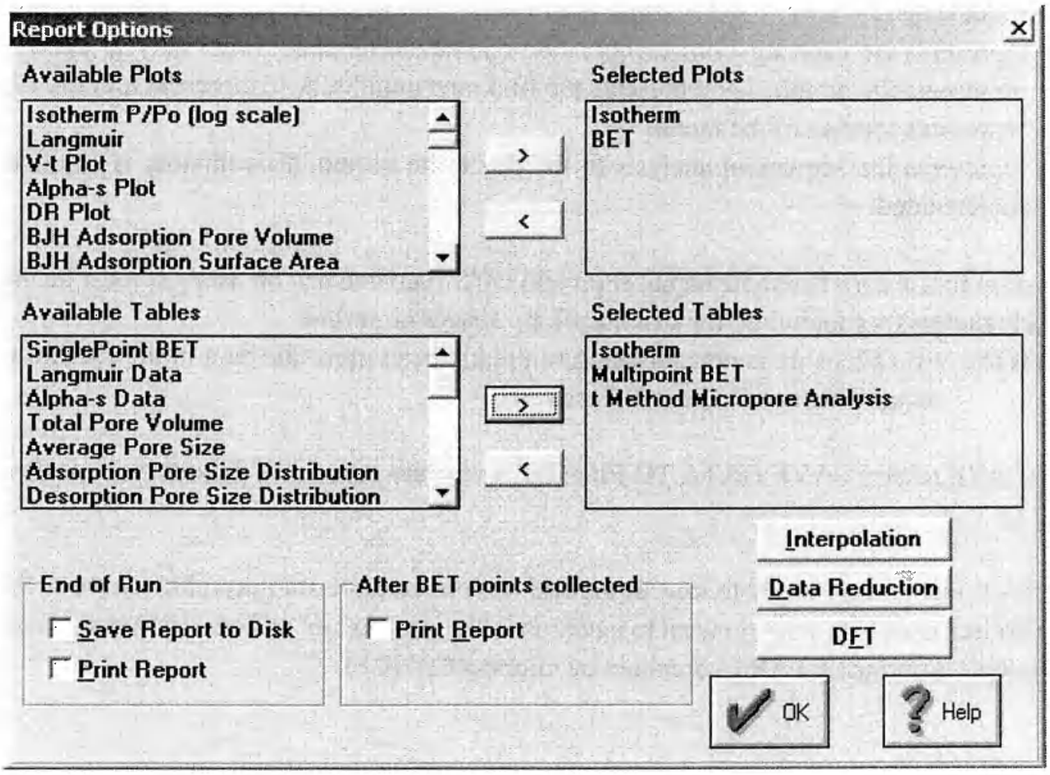
If you want to use a different filename, any valid DOS filename can be used. It must be no more than 8 characters (not including the extension), no spaces or period.

CAUTION: If a filename is entered that has already been used, the data in the old file will be overwritten and cannot be recovered.

RE-CREATE resets "SAVE DATA TO FILE ID" to the next available default name as described above.

START - When you are ready to start an analysis on one or more stations, click on the green start button. Select which station you want to have run in the pop-up box and confirm your selection by clicking OK. Abort the START command by clicking CANCEL.

EDIT REPORT OPTIONS - Use this to predefine the format of an analysis report for each sample.



Selected Plots
Isotherm
BET

Selected Tables
Isotherm
Multipoint BET
t Method Micropore Analysis

End of Run
☐ Save Report to Disk
☐ Print Report

After BET points collected
☐ Print Report

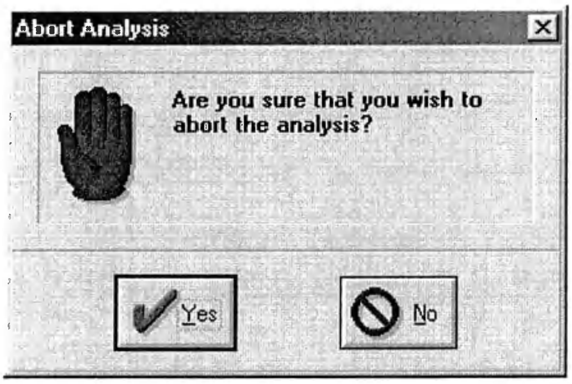
Select from the list of AVAILABLE PLOTS and TABLES listed on the left side and transfer to the SELECTED PLOTS and TABLES on the right by clicking on the > button. Plots and tables can be removed from the selected list by highlighting them and clicking on the < button.

In addition, INTERPOLATION, DATA REDUCTION and DFT information can be selected and set. See the appropriate section in the DATA REDUCTION section of this manual

You can also elect to automatically save the report to disk (tables only) and/or print the entire report at the end of the run. In addition, the BET report can be printed as soon as all BET points have been measured. Just check the appropriate boxes.

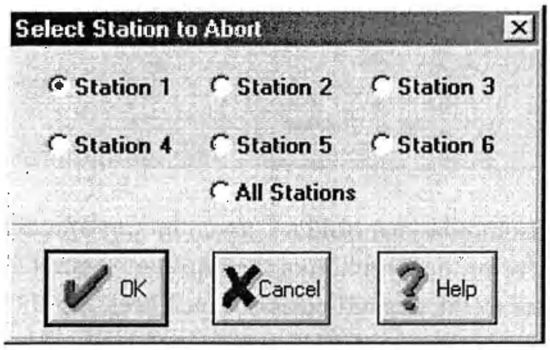
ABORT ANALYSIS

To prematurely end an analysis, select Abort Analysis from the Analysis drop down menu. This action must be confirmed, thus preventing accidental aborts.



Are you sure that you wish to abort the analysis?

Click [YES] to confirm or [NO] to cancel. If you choose [YES] another box appears for you to select the station on which the analysis will be aborted.



● Station 1 ○ Station 2 ○ Station 3
○ Station 4 ○ Station 5 ○ Station 6
○ All Stations

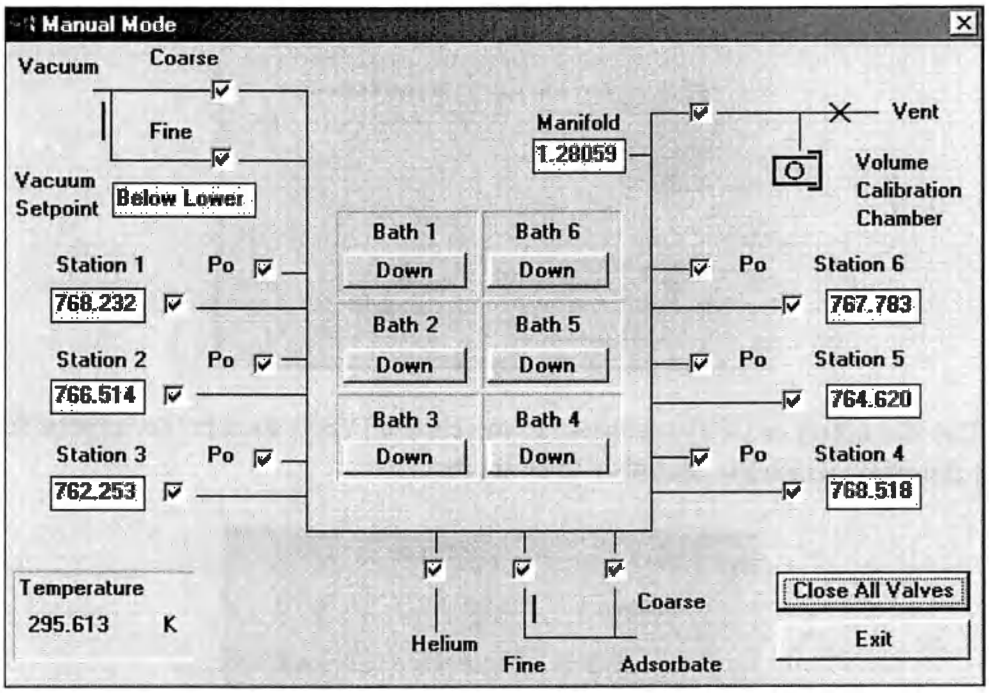
If desired, all stations can be aborted at once. Click on [OK] to begin the abort routine. Click on [CANCEL] to exit without aborting an analysis.

OPERATIONS

MANUAL MODE (NOT FOR ROUTINE USE!)

This gives you complete manual control of the system's valves and Dewar flasks and the ability to display the system temperature and pressures. Entry into the manual mode while an analysis is in progress is not recommended, since this mode stops automatic processing and can allow a system overpressurization. It should not be used for routine operation of the instrument or by people not thoroughly familiar with the instrument. *Access to Manual Mode during analysis can corrupt data and improper valve manipulation may cause damage to instrument*.

When the manual mode is selected the state of each valve (☐-open, ☑-closed) and the direction of the liquid nitrogen bath (up, down) are displayed. A typical display of the manual mode for the AUTOSORB-6 is shown below:



Vacuum Setpoint: Below Lower
Manifold: 1.28059
Station 1: 768.232
Station 2: 766.514
Station 3: 762.253
Station 4: 768.518
Station 5: 764.620
Station 6: 767.783
Temperature: 295.613 K

The pressures of the stations and the manifold are given in mm of mercury and the temperature in kelvin. The state of any valve or the direction of the liquid nitrogen Dewar flask may be manually altered by moving the cursor to the desired position, then pressing the left mouse button. All the valves can be closed at once by selecting [CLOSE ALL VALVES]. The Turbo Pump button will be displayed only if the krypton or micropore option is installed.

To exit from the manual mode, Click on [EXIT]. All valves and the Dewar flasks will be restored to their original status, i.e. that prior to entering manual mode.

INSTRUMENT CALIBRATION

Since all the results obtained on the AUTOSORB are based on the volume of the manifold, it is a good practice to calibrate it occasionally. The manifold cannot be calibrated while an analysis is running.

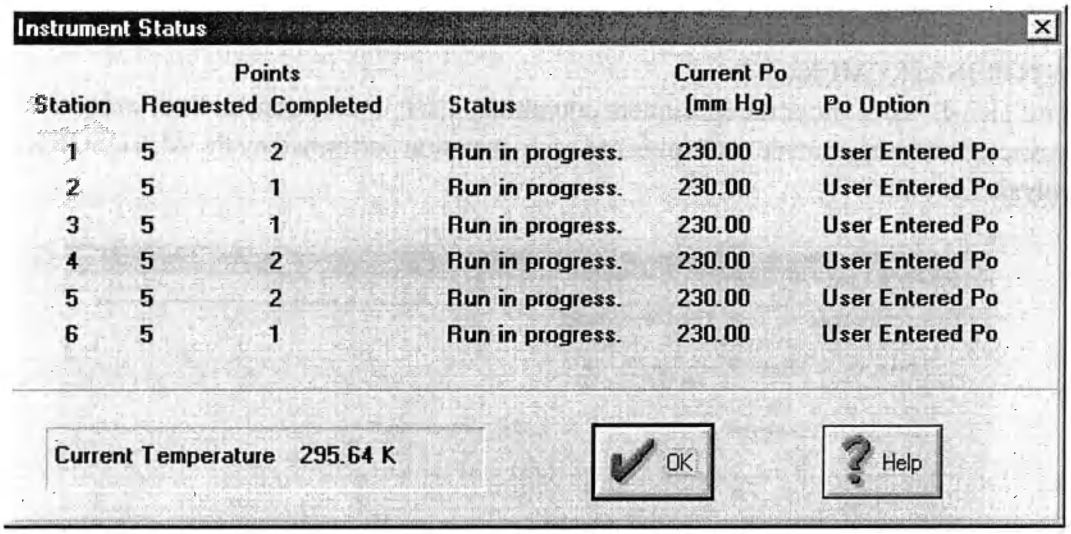
Confirm that you do want to recalibrate the manifold. When prompted, enter the volume of the calibration sphere (Std. Sphere=56.5592 cc). Fully seat the cover with its white fiduciary marks aligned, and press any key. When prompted, place the calibration sphere into the chamber and again press any key. The system will complete the calibration and display the following:

CALCULATED MANIFOLD VOLUME = XX.XX OLD MANIFOLD VOLUME = XX.XX

1. USE OLD VALUE
2. USE NEW VALUE
3. ENTER NEW VALUE
PRESS SELECTION (1-3)

Choose 1 to retain previous calibration value; 2 to accept the value just acquired, or another value can be entered by choosing 3. This last entry is useful for using an average of several calibration values.

INSTRUMENT STATUS (F8)
Press <F8> or select [INSTRUMENT STATUS] from the OPERATIONS drop down menu to produce a system status report.



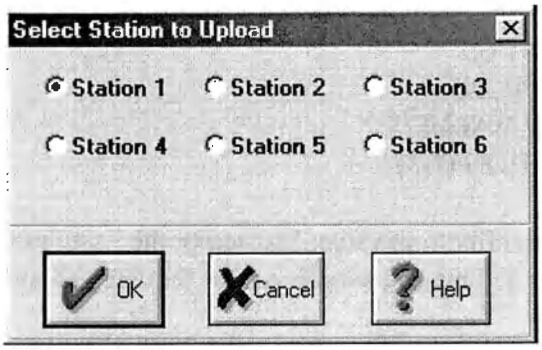
	Points			Current Po	
Station	Requested	Completed	Status	(mm Hg)	Po Option
1	5	2	Run in progress.	230.00	User Entered Po
2	5	1	Run in progress.	230.00	User Entered Po
3	5	1	Run in progress.	230.00	User Entered Po
4	5	2	Run in progress.	230.00	User Entered Po
5	5	2	Run in progress.	230.00	User Entered Po
6	5	1	Run in progress.	230.00	User Entered Po

Current Temperature 295.64 K

Click [OK] to close the Instrument Status display.

UPLOAD DATA (F9)

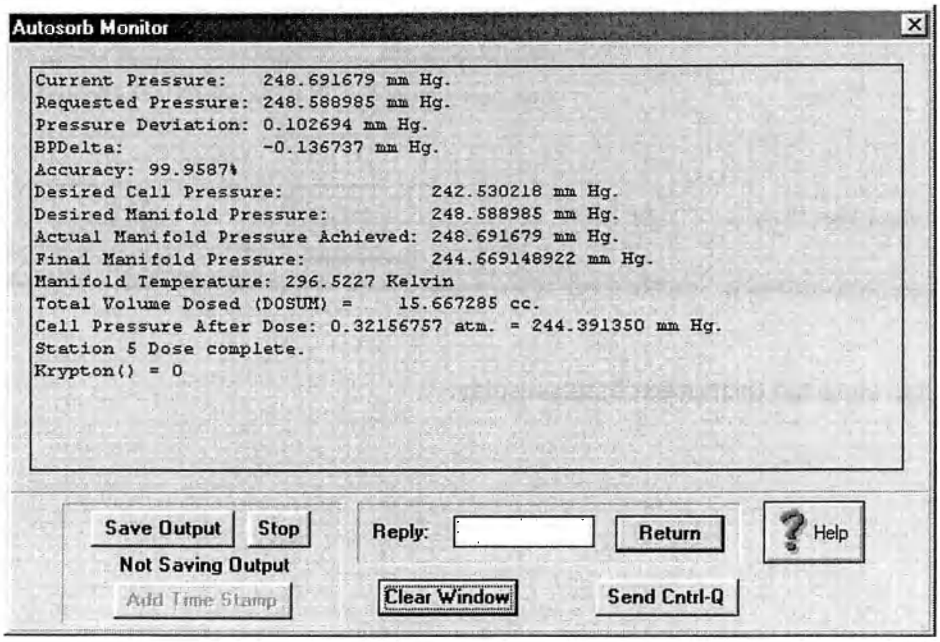
Press F9 or select [UPLOAD DATA] from the operations drop down menu to display the SELECT STATION TO UPLOAD dialog box.



Click on the desired station and then on [OK] to transfer the data currently stored in the Autosorb to the PC. A graph of the isotherm will be displayed and the data file saved. Any desired data reduction function can be performed (if the data for the function have been acquired and properly tagged).

MONITOR INSTRUMENT

Press <CTRL-B> to monitor the instrument operation, in detail, in real time. Its primary function is diagnostics; however, it can be used to record each operation performed by the AUTOSORB during an analysis.



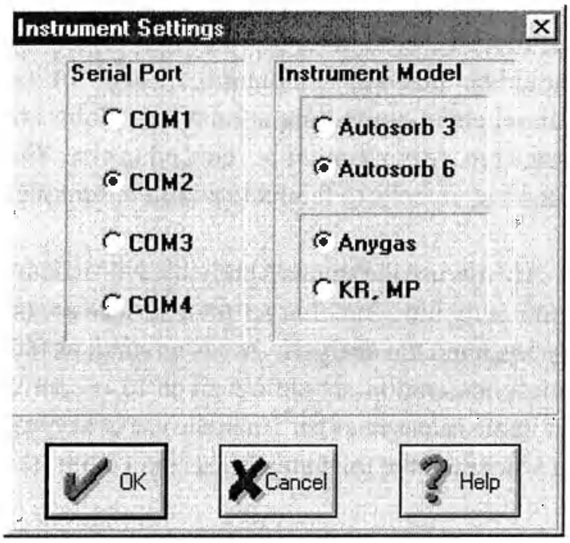
```
Current Pressure:   248.691679 mm Hg.
Requested Pressure: 248.588985 mm Hg.
Pressure Deviation: 0.102694 mm Hg.
BPDelta:            -0.136737 mm Hg.
Accuracy: 99.9587%
Desired Cell Pressure:              242.530218 mm Hg.
Desired Manifold Pressure:          248.588985 mm Hg.
Actual Manifold Pressure Achieved: 248.691679 mm Hg.
Final Manifold Pressure:            244.669148922 mm Hg.
Manifold Temperature: 296.5227 Kelvin
Total Volume Dosed (DOSUM) =    15.667285 cc.
Cell Pressure After Dose: 0.32156757 atm. = 244.391350 mm Hg.
Station 5 Dose complete.
Krypton() = 0
```

This box also appears during AUTOSORB boot-up.

Save the information to the PC by clicking [SAVE OUTPUT] and type in a filename. This information will be valuable if it is necessary to call QUANTACHROME with a question about the operation of the instrument. The [SAVE OUTPUT] can be discontinued at any time by clicking on [STOP]. If a file is saved under an existing name, the new messages will be added to the end of that existing file. This allows you to exit and reenter the monitor window while saving a single log file.

INSTRUMENT SETTINGS

When selected from the [OPERATIONS] drop down menu, the type of instrument (model) communication port can be viewed and corrected if necessary



Instrument Settings

Serial Port
○ COM1
● COM2
○ COM3
○ COM4

Instrument Model
○ Autosorb 3
● Autosorb 6

● Anygas
○ KR, MP

When all selections are correct, click on [OK] to save the selections and exit or, to exit without making changes to the instrument settings, click on [CANCEL].

V. SAMPLE PREPARATION AND CELL SELECTION

A. OVERVIEW

Selecting a Sample Cell
Choosing a Degas Temperature
Degas Time and Testing for Complete Degassing
Backfill Gas and Unloading
Elutriation and Its Prevention
Available Cells
Autosorb 3 Degaser

B. SELECTING A SAMPLE CELL

Stem diameter: Choose the narrowest diameter cell that will comfortably admit the sample. For example, a fine powder should be analyzed in a 6mm o.d. (4mm i.d.) stem cell. Larger particles such as granules, and small pellets might require a 9mm o.d. (7mm i.d.) diameter stem. Use the 12mm o.d. stem cells for large pieces that cannot be reduced in size. Of course, cohesive powders may be analyzed in 9 or 12mm stem cells to facilitate addition, removal and cleaning.

Sample amount/Bulb Size: Always use the smallest bulb that will accommodate the optimal amount of surface area, i.e. 5 - 20 m^2 using nitrogen. Larger total surface areas can certainly be analyzed, but they may unnecessarily lengthen the analysis. Areas as small as 0.5 to 1.0 m^2 can be analyzed using nitrogen, but careful consideration should be given to proper degassing and equilibrium criteria. If the total area available is less than $1m^2$, then the use of krypton gas should be considered, and should always be used whenever the total area is less than $0.5m^2$ (krypton capable units only).

Wider stems and larger bulbs can be beneficial in reducing elutriation, see below.

Filler rods are used to reduce void volume of the cell and therefore enhance sensitivity and accuracy. They should not be used whilst degassing, but only during analysis.

See also subsection G.

C. CHOOSING A DEGAS TEMPERATURE

Samples should be degassed at the highest temperature (up to 350 degC) that will not cause a structural change to the sample. This will accelerate the degassing process. Oxides such as alumina and silica can normally be safely degassed at 350 degC. Most carbon samples can also be degassed at 300 degC, as can calcium carbonate. Many hydroxides must be degassed at a lower temperature. Degassing organics must be performed with care since most have quite low softening or glass transition points. For example, magnesium stearate, a common pharmaceutical formulating compound, should be degassed at 40 degC according to the USP.

Loosely bound water ("wet water") will be lost at relatively low temperatures under the influence of vacuum, but strongly bound surface water might require surprisingly high temperatures. Many zeolites, for example, will retain significant quantities of water in their micropores up to 300+ degC.

Use technical reference literature such as the Handbook of Chemistry and Physics (CRC, Boca Raton, Florida) and standard methods such as those published by ASTM to guide your selection of an appropriate degassing temperature.

If you have access to thermal analysis equipment, especially gravimetric, an analysis should be conducted on a separate aliquot of material prior to degassing on the Autosorb. A suitable degassing temperature would be that which lies in a plateau, or weight-stable region, of the thermogram. Ideally, the thermal analysis should be conducted under vacuum. In general, too low a degassing temperature will cause lengthy preparation, and may result in lower than expected surface areas and pore volumes.

Too high a temperature can cause irreversible damage to the sample, which can result in a decrease in surface area due to sintering, or an increase in surface area due to a thermally induced decomposition

D. DEGAS TIME AND TESTING FOR COMPLETE DEGASSING

Time for complete degassing, that is complete removal of unwanted vapors and gases adsorbed on the sample surface, can only be properly determined by conducting a degas test which is built in to the Autosorb software. As a general guideline however, three hours (at temperature) should be considered a reasonable minimum. IUPAC recommend no less than sixteen hours, which can be conveniently achieved overnight. Samples that require low temperatures generally require the longest outgas times. However, the USP recommended degassing period for magnesium stearate is just two hours at 40 degC.

A sample can be considered ready for analysis when the sample passes a degas test of no more than 50 microns Hg per minute (at elevated temperature). A sample that cannot pass the same criterion at room temperature may not be able to be initialized by the Autosorb when installed in the analysis station. Remember, the Autosorb must be able to pull, and hold, a high vacuum in the sample cell in the presence of sample. A contaminated degas station may give artificially high degassing rates during test. You can establish the background pressure rise of a degas station by *loading* and *testing* a dowel pin or clean and empty sample cell. A clean system should be able to pass a 20 micron Hg per minute test.

Always degas without a filler rod in the cell.

E. BACKFILL GAS AND UNLOADING

Preferably, the adsorbate should be used as backfill gas to prevent or minimize buoyancy errors. A sample cell will weigh less when filled with helium than when filled with air or nitrogen. The error introduced is approximately 1mg per mL of cell volume. This can be significant when using extremely small sample weights (< 50mg).

The heating mantle should be switched off using the toggle switch on the front of the Degasser some time prior to removing the sample from the Degasser. Allow the mantle to cool below 100 degC before removing the mantle and sample. Remember, heating mantle clamps may be very hot. A sample cell which feels only warm to the touch whilst still under vacuum can be much hotter to the touch when backfilled with gas. This is particularly true if you are degassing a large mass of metal sample. Exercise caution! A warm sample cell can also introduce weighing errors. The sample cell should be allowed to cool to room temperature before weighing. If sample throughput permits, cool thoroughly while attached to the Autosorb, otherwise remove and transfer to a desiccator.

F. ELUTRIATION AND ITS PREVENTION

Elutriation, or loss of powder out of the sample cell, is caused by too rapid a gas flow out of the cell. It is most problematical for low-density samples, fumed silica for example. Always backfill the manifold with gas before opening the valve to the cell (be sure to close both vacuum valves and the valves on samples already loaded before backfilling the manifold). Open the fine vacuum valve slowly. Close it immediately if you observe elutriation. Use the needle valve to restrict the fine vacuum even further. Try again. Eventually you will be able to open the coarse vacuum valve and proceed with degassing normally.

Wider cell stems and larger cell bulbs can be beneficial in reducing elutriation. Wider stems reduce the velocity of the gas leaving the cell when evacuation begins and thus it is less likely to entrain powder particles and transport them upwards and out of the cell. The presence of a filler rod significantly increases gas velocity because of the narrowing of the internal dimensions and can exacerbate elutriation. In problematical cases, the filler rod may be dispensed with during analysis, but some loss of resolution and/or sensitivity may result. A larger bulb than necessary significantly reduces gas velocity in the immediate vicinity of the sample (but does increase void volume) and allows the sample to move around without being entrained in the higher velocity up the stem portion.

The most dramatic elutriation problems are encountered during degassing of *damp, light* powders. As the sample heats from ambient, the pressure over the sample decreases due to the action of the vacuum. At some point the water *flashes* into steam. This rapid expansion of gas volume drives powder out of the bulb and up the stem of the cell. This condition can be reduced or eliminated by (i) pre-drying the samples in a conventional drying oven and (ii) raising the temperature of the heating mantle in 20 degree steps. It is recommended that the temperature be *paused* at 60 degC for 30 B 60 minutes under vacuum to allow for a milder removal of moisture before increasing the temperature to 80degC, then 100degC and finally maximum degas temperature.

Degas stations are fitted with filters that are installed as part of the ***bulkhead adapters***. If these become contaminated, or it is desirable to change them for a finer filter, they can be easily removed and cleaned, or replaced entirely. A further flow restriction in the form of a tight fitting 20 micron filter called a *Cell-Seal* (p/n 01509-7150-1) can be inserted into the stems of 9mm sample cells.

In the most difficult cases, and the aforementioned methods have not eliminated the problem it might be necessary to insert a small glass wool plug into the cell stem. This can be held in place between two halves of a cut-in-two glass filler rod. This is the only time that a filler rod should be used in the degasser.

G. AVAILABLE CELLS

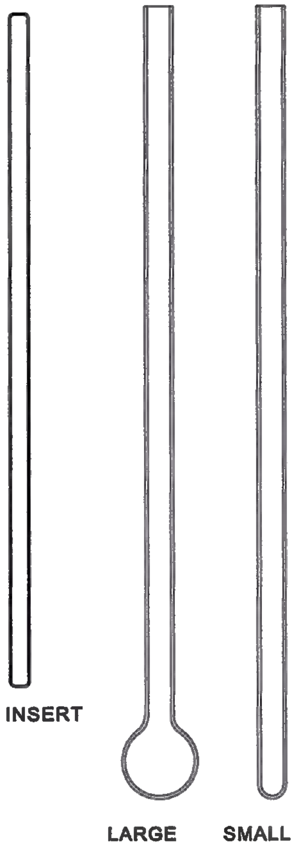
Standard sample cells and parts for use with the AUTOSORB			
Part	Part Numbers		
	6 mm	9 mm	12 mm
Cell, bulbless	74098	74052	74054
Cell, small bulb	74027		74059
Cell, large bulb	74028	74053	74055
Rod with cap	74058-7	74058-8	74058-9
Rod without cap	74058-7NM	74058-8NM	74058-9NM
Adapter sleeve	04000-3499-1	04000-3499-2	04000-3499-3

Sample cells for use with the AUTOSORB are described below:

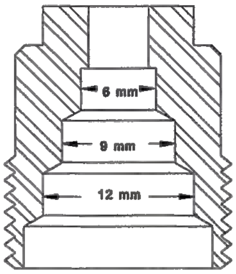
1. PELLET CELL, Small - used for small quantities of pellet samples or powders which do not adhere to the walls of the stem.

PELLET CELL, Large - used for pellet or powder samples when larger quantities are required for an analysis.

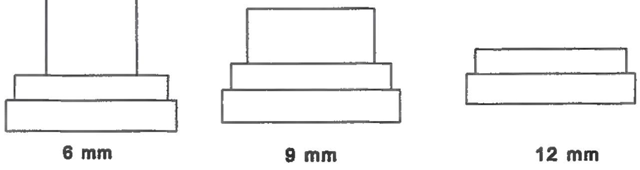
The small and large pellet cells are supplied with stem diameters of 6, 9 and 12 mm. The appropriate sleeve, insert (filler rod) and O-ring must be used with each cell.



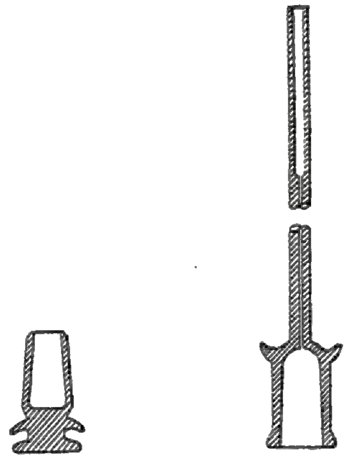
PELLET CELLS



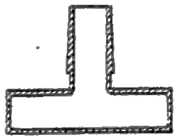
ADAPTER SLEEVES



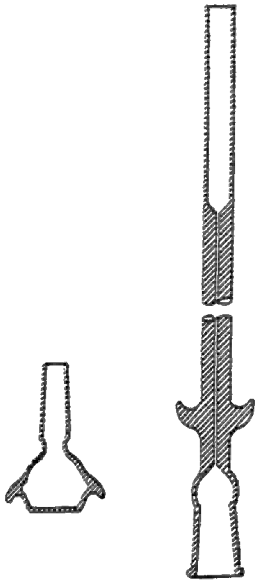
2. POWDER CELL (Part No. 74026) used for fine powders, which are placed in the bulb of the cell and connected to a 1 mm cell stem (Part No. 74024). The sample bulb is 10 X 28 mm.

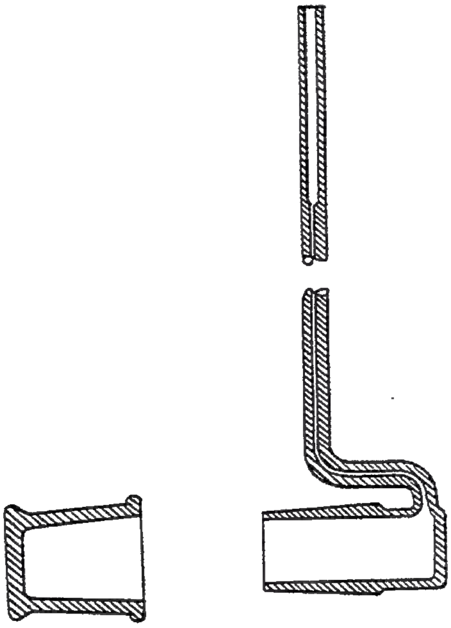


3. T-CELL BODY (Part No. 74023) used for large quantities of powder or pellets with low surface area materials. A 1 mm cell stem (Part No. 74024) is used with the T-cell. The cell dimensions are 10 X 50 mm.

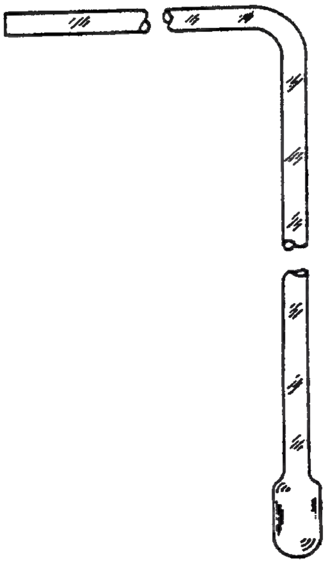


4. MICRO POWDER CELL (Part No. 74034) used for fine powders with high surface areas to minimize the void volume. The bulb volume is about 0.8cc.

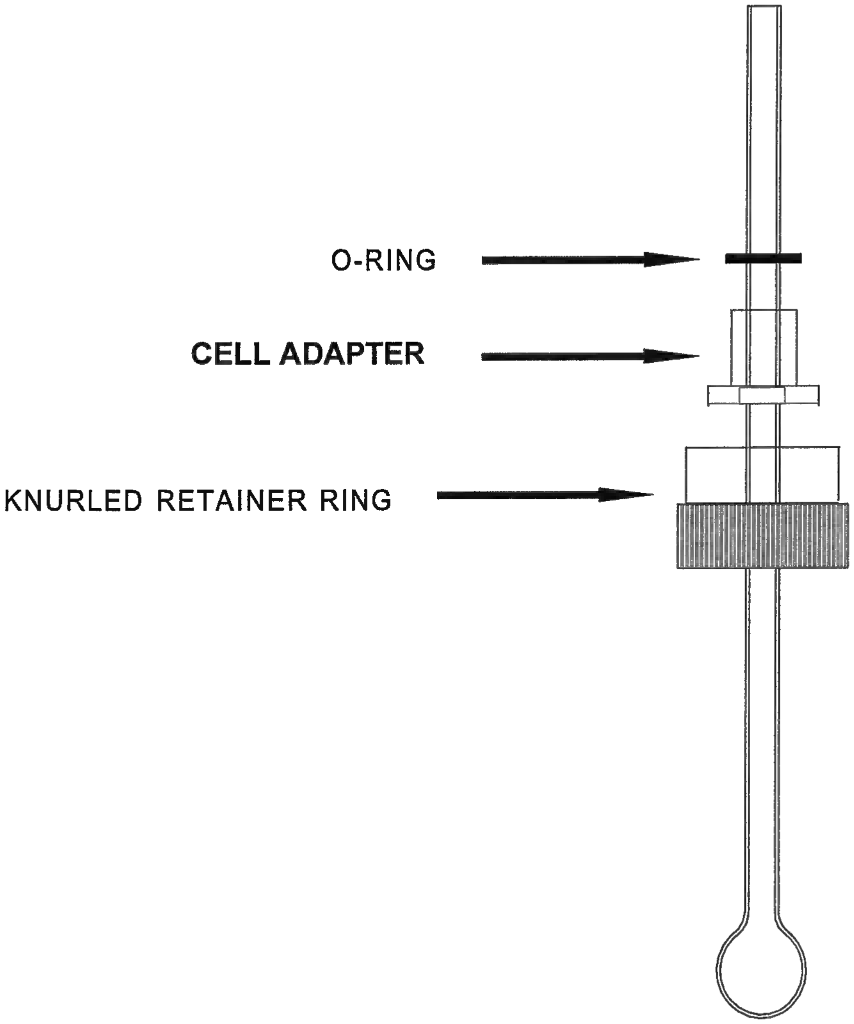




5. MACROCELL (Part No. 74030)-used for large solid pieces of sample. A 1 mm-cell stem (Part No. 74031) is used with the macrocell. The cell dimensions are 18 X 40 mm. This cell requires a wide mouth Dewar, P/N 74071.



6. P_0 CELL (Part No. 74035) used to measure the saturated vapor pressure of adsorbate during an analysis.



SAMPLE CELL ASSEMBLY

H. AUTOSORB 3 DEGASSER

Note: A separate six station degasser is available for use with the AUTOSORB-6 or to provide supplemental degassing stations for the AUTOSORB-3.

DEGASSING

Sample degassing is manually controlled by the toggle valves above the degassing stations on the left side of the AUTOSORB-3B. Up to three samples can be simultaneously degassed. When not in use, both the coarse and fine valves should be closed.

LOADING A SAMPLE

1. Attach a heating mantle to the sample cell using the supplied clamp and put the cell in an available station. Connect the power and thermocouple leads to the appropriate outlets on the panel.

NOTE: Glass heating mantles should not be used above 300°C. For temperatures over 300°C up to 400°C quartz mantles and sample cells are available.

2. Close all valves including the fine vacuum adjust.
3. Open the helium valve for approximately 5 seconds and then close it.
4. Open the desired station valve.
5. Open the fine vacuum valve (for fine powders).
6. Open fine vacuum adjustment valve slowly (for fine powders).
7. Set the degassing temperature using the digital pots. It may be desirable to set a temperature lower than the final value to prevent a sudden release of water vapor. Then gradually bring it up to the final degassing temperature.

Note: For pellets open both the fine and coarse valves at the same time. The fine vacuum adjustment is used to prevent powder from elutriating into the degasser manifold.

TESTING A SAMPLE

1. Close the valves to all stations that are not being tested.
2. Close the fine and coarse vacuum valves.
3. Look at the vacuum gauge. If the pressure increases the sample is not completely degassed.
4. To resume degassing open both vacuum valves and the valves to the other stations being degassed.

REMOVING A SAMPLE

1. Turn the heating mantle off by setting the digital pot to 000.
2. Close all sample station valves and both vacuum valves.
3. Open the station valve from which the sample cell is to be removed.
4. Open the helium valve for approximately 5 seconds.
5. Close the helium valve.
6. Close the station valve.
7. Remove the heating mantle and transfer the sample cell to an analysis station for testing.
8. Evacuate the manifold before opening the valves to any other stations on which degassing will continue.

VI. ROUTINE MECHANICAL MAINTENANCE AND SERVICE

A. GAS FLOW RATES

1. For all gasses, the input pressure should be set to 10 PSIG (0.7301 Kg/cm^2 or 68.95 Kpa). .
2. To test, adjust regulator well below 10 PSIG.
3. Enter manual mode. Open coarse adsorbate. Observe pressure on front of instrument. If it rises above 1200 mm Hg, Open and close the coarse vacuum valve until the pressure stays below 1000 mm Hg.
4. Increase regulator, until the pressure on the front of the instrument is about 1225 to 1275 mm Hg. Note that 1277 mm Hg is 10 PSIG, 1225 is 9 PSIG, 1177 mm Hg is 8 PSIG, 1018 is 5 PSIG. Observe the pressure on the regulator, Note any offset between 10 PSIG and the reading. Warning: Never adjust the pressure above 1300 mm Hg in this mode.
5. Repeat steps 2-4 with the helium regulator.

When the gas tanks or regulators are changed, or if unusually long times are needed to achieve a desired relative pressure, it may be necessary to adjust the flow rates. Follow the procedure below to determine if the flow rates are within the proper range and adjust if necessary.

The flow rates for helium and nitrogen are controlled by three needle valves in the top compartment of the instrument. When looking into the compartment from the front of the AUTOSORB the helium needle valve is on the left and the nitrogen valves are on the right. The fine nitrogen needle valve is toward the front and the coarse nitrogen valve is toward the rear.

1. To adjust the flows, select the AUTOSORB manual mode from the OPERATIONS drop down menu. (See *Manual Mode* in the OPERATIONS section of this manual.)
2. Open the coarse vacuum valve, close the fine vacuum valve, the Cal valve and all the cell valves.
3. Now open the gas valve for the flow which is to be adjusted (Helium, Fine Nitrogen or Coarse Nitrogen).
4. Close the coarse vacuum valve and note the change in the manifold pressure each time the reading is updated on the digital display on the front panel.
5. Open the coarse vacuum valve before the pressure exceeds 700 mm Hg.
6. Adjust the appropriate needle valve so that each update on the screen shows a change of manifold pressure readings of 30 to 40 mm for helium, 1 to 2 mm for fine nitrogen and 10 to 20 mm for coarse nitrogen.
7. Repeat this process of closing the coarse vacuum valve, noting the change in the manifold pressure, then opening the vacuum valve and adjusting the needle valve.
8. When the correct flow is set, close the gas valve and repeat for the next gas valve.

The following procedure is used to set the fine vacuum rate needle valve, located in the rear of the top compartment of the AUTOSORB.

9. Close the fine and coarse vacuum valves.
10. Open the helium valve and allow the pressure to increase until 760 mm is displayed on the digital meter. Then close the helium valve.
11. Open the fine vacuum valve and adjust the fine vacuum needle valve until the meter displays a decrease in pressure from 760 to 76 mm in about 20 seconds. If it is found that fine particles are elutriated during the evacuation of a sample cell, the fine vacuum rate needle valve can be adjusted to take a longer time (up to 60 seconds) to reach 76 mm.
12. When complete, exit the manual mode and return to the main menu.

B. LEAK CHECKS

This procedure will test for leaks in the manifold using the main manifold transducer pressure reading.

1. Go into manual mode.
2. Close both vacuum valves.
3. Open cell valve 1 and then open station 1 to ambient.
4. Record reading on screen for manifold pressure.
   Result________________mm
5. Close cell valve 1.
6. Let the AUTOSORB stay in this state for approximately 1 hr. There will be a rise or fall in pressure if there is a leak. Continue to test to localize the leak.
   Starting pressure________________mm
   Last pressure reading__________________mm
7. Disconnect the nitrogen input line from the AUTOSORB.
8. Close both vacuum valves.
9. Bring the manifold to ambient using steps 2 and 3.
10. Let the AUTOSORB stay in this state for 1 hr. There will be a rise in pressure if there is a leak in helium valve. If there is a rise in pressure, change the helium valve.
    Starting pressure_________________mm
    Last pressure reading__________________mm
11. Reconnect the nitrogen input line to AUTOSORB.
12. Close both vacuum valves and bring the manifold to ambient pressure using steps 2 and 3
13. Let the AUTOSORB stay in this state for 1 hr. There will be a rise in pressure if there is a nitrogen leak. If there is a rise in pressure, change both nitrogen valves.
    Starting pressure___________________mm
    Last pressure reading_________________mm
14. Bring the manifold up to approximately 800 mm of helium and let the AUTOSORB stay in this state for 1 hour. Look for a drop in pressure. If there is a drop in pressure, change both vacuum valves.
    Starting pressure_________________mm

Last pressure reading__________________mm

15. Open the calibration chamber valve and both vacuum valves. Let the system pump down to 0 mm.
16. Close the calibration chamber and fill the manifold with approximately 800 mm of helium. Let the unit stay in this state for 1 hr. Look for a drop in pressure. If the pressure drops, change the calibration valve.
    Starting pressure__________________mm
    Last pressure reading__________________mm
17. Open both vacuum valves and pump the manifold down to 0 mm.
18. Close both vacuum valves and open the calibration chamber.
19. Fill the manifold with approximately 800 mm of helium and then close the calibration chamber.
20. Open both vacuum valves and pump the manifold to 0 mm. Then close both vacuum valves. Let the unit stay in this state for 1 hour. Look for a rise in the manifold pressure. If there is a rise in pressure, change the calibration valve.
    Starting pressure__________________mm
    Last pressure reading__________________mm
21. Plug all the stations. Open the vacuum and cell valves. Close the vacuum valve and record the pressure. If the pressure increases, check the O-ring for the station cell.
22. To test for leaks in a cell valve, close the cell valve and open the station to ambient. Open the vacuum valve. If the pressure falls, there is a leak in the cell valve. Change the cell valve.

APPENDIX 1

SYSTEM ERROR MESSAGES

PROBLEM WITH BATH - this error message indicates that the system is not receiving a valid bath status from the indicated station. This could be caused by an electrical or mechanical problem with the bath drive on the station, but it is more likely to be caused by a loose or missing thermistor probe, a Dewar flask that has not been filled with liquid nitrogen or a missing Dewar flask.

LEAK TEST FAILED - indicates that the station whose number is shown failed the leak test. The most likely causes of this message are a poorly outgassed sample, a leak around the cell connection or a leak in the vacuum grease fittings on the sample cell.

ABORTED LOW LN_2 - indicates that the station has been aborted because the liquid nitrogen has dropped below the usable level. If the liquid nitrogen level in the Dewar flask appears adequate, it may indicate a loose or damaged thermistor probe.

POWER LOSS HAS OCCURRED - indicates that a power outage or loss of vacuum pump status has occurred, but the system is now back in full operation.

OVERPRESSURIZATION HAS OCCURRED - indicates that the specified station has over-pressurized and all stations have been or are being aborted. If an overpressurization occurs during a power loss the system will respond in the described manner when power is restored but will be unable to determine the station which caused the overpressurization.

APPENDIX 2

P/P_0 TOLERANCE AND EQUILIBRATION TIME

NOTE: For the sake of clarity this discussion will refer only to adsorption data points. Desorption data points are acquired in the same manner except in the opposite direction.

TOLERANCE	ADSORPTION TOLERANCE		DESORPTION TOLERANCE	
	0 to 0.1	0.1 to 1	0.1 to 0	1 to 0.1
0	+.00003 -.00001	+.003 -.001	+.00001 -.00003	+.001 -.003
1	+.00006 -.00002	+.006 -.002	+.00002 -.00006	+.002 -.006
2	+.00009 -.00003	+.009 -.003	+.00003 -.00009	+.003 -.009
3	+.00012 -.00004	+.012 -.004	+.00004 -.00012	+.004 -.012
4	+.00015 -.00005	+.015 -.005	+.00005 -.00015	+.005 -.015
5	+.00018 -.00006	+.018 -.006	+.00006 -.00018	+.006 -.018
6	+.00021 -.00007	+.021 -.007	+.00007 -.00021	+.007 -.021
7	+.00024 -.00008	+.024 -.008	+.00008 -.00024	+.008 -.024
8	+.00027 -.00009	+.027 -.009	+.00009 -.00027	+.009 -.027
9	+.00030 -.00010	+.030 -.010	+.00010 -.00030	+.010 -.030

Note: Instruments with the krypton option will use the low pressure tolerance values when the cell pressure is below 0.1 atmospheres. The range automatically switches to the high pressure tolerances when the cell pressure goes over 0.1.

The minimum relative pressure and interval that can be specified is 0.00001.

The minimum cell pressure that will be accepted by the instrument is 2×10^{-6} atmospheres.

A dose on a sample is performed in the following manner: the pressure in the cell is measured, the manifold pressure is increased to an amount such that when the cell valve is opened to the manifold the resulting pressure in the cell will be equal to the desired relative pressure plus the P/P_0 tolerance, assuming that no adsorption occurs. For example, if the desired relative pressure is 0.100 and a P/P_0 tolerance of 0 was selected, the manifold will build to a pressure which, when connected to the cell, will result in a cell pressure of 0.103 if no adsorption occurs. If the selected P/P_0 tolerance is 9, then the system will attempt to achieve a cell pressure of 0.130. Therefore, the larger the P/P_0 tolerance the larger the dose and consequently the shorter the analysis time.

When the manifold has reached its target pressure, the cell valve will open for 8 seconds to allow adsorption from the larger combined cell and manifold volumes and then the cell will be isolated for 15 seconds after which the pressure in the cell is measured on the cell transducer. If the cell pressure has dropped below the desired relative pressure the cell is scheduled for another dose; otherwise, the cell is scheduled for an equilibration check in one minute.

During equilibration the pressure in the sample station is measured every six seconds. The pressure reading is stored in memory and compared against the lower limit of the P/P_0 tolerance (for example with a desired relative pressure of 0.100 and a P/P_0 tolerance of 9 the lower limit is 0.09). If the pressure is below the lower limit a dose is scheduled. Otherwise the pressure is checked for a valid equilibrium condition. A sample is considered to have reached equilibrium when the pressure changes less than 0.0008 atm. for the period of time selected by the operator of between 1 and 99 minutes. For example, if an equilibration time of 2 was specified then each time the pressure is checked during equilibration the pressure reading is compared to the reading taken 2 minutes earlier. This will continue until the pressure in the cell drops below the lower limit of the P/P_0 tolerance or the difference between the two readings is less than 0.0008 atm. The data point is then stored and dosing will begin for the next data point.

If the cell does not meet the equilibrium requirements described above, the target cell pressure for subsequent doses is increased in order to bring the sample cell to equilibrium sooner. However, the time it took to drop below the lower tolerance limit is also taken into consideration so that an overdose does not occur and the sample cannot equilibrate above the upper tolerance limit.

APPENDIX 3

ANALYSIS GAS SELECTION

The AUTOSORB is capable of measuring the adsorption of any non-corrosive gas. In order to obtain meaningful data, several parameters must be known about the adsorbate.

Prior to reducing the void volume (V_v) to standard conditions, the measured volume is corrected for nonideality. Using V'_v as the corrected void volume, the correction for nonideality is

$$V'_v = V_v \left(1+\alpha P \right)$$

Table 1 includes the alpha value for several gases at various temperatures.

Note: When entering the alpha correction factor do not enter the exponent. The computer will multiply the entered value by 10^{-5}.

Table 1 also includes the cross-sectional areas and molecular weights of several gases.

The coolant used should provide a saturated vapor pressure, P_0, of 10 mm or greater. If it is necessary to use an adsorbate and coolant with a lower P_0 the user should enter the saturated vapor pressure during initialization of the run.

CAUTION: When changing adsorbates be sure to evacuate the adsorbate lines in the AUTOSORB (manual mode) and then purge them with the new gas.

TABLE 1

GAS	TEMP [°C]	α FACTOR X 10^{-5} [mm Hg^{-1}]	CROSS SECTIONAL AREA [$Å^2$/molecule]	MOLECULAR WEIGHT [g/mol]
Ar	-195.8	11.4	14.2	39.948
	-183	3.94		
CO_2	-78	2.75	19.5	44.01
	-25	1.55		
	0	0.91		
CO	-183	3.42	16.3	28.01
Kr	-195.8	3.00	20.5	83.80
N_2	-195.8	6.58	16.2	28.0134
	-183	3.78		
O_2	-183	4.17	14.1	31.9988
C_4H_{10}	0	14.2	46.9	58.12
	25	4.21		

BATH LEVEL SENSORS

The AUTOSORB is supplied with thermistors that will detect and control the level of the bath if liquid nitrogen is used as the coolant. See also Appendix 6. When using adsorbates other than N_2, it may be necessary to use a different coolant bath. In this instance, Quantachrome can supply level sensors for coolants in the temperature range of 200 K such liquid argon 87 K (P/N 00080-AR-RTD) as dry ice/acetone (P/N 00080-3190-RTD) and 273 K i.e. ice water (P/N 00080-H2O-RTD)

APPENDIX 4

POWER-ON DIAGNOSTICS

When the AUTOSORB is turned on the system does several self tests. First, the system does a safety check of all the bath drives. If the bath drive on any station is not in the down position the station number and the message "BATH DRIVES HAVE UNEXPECTED STATUS" will be displayed on the video terminal. The system will attempt to pull a vacuum on those stations before sending the baths down. If there is no danger of overpressurization, follow the directions on the video terminal to stop pumping on the station and continue the start-up process.

Second, the system will perform a test of its read-only memory (ROM). If the system finds a bad ROM, a letter code for the ROM will be displayed on the video terminal along with a warning message. Copy the letter (or letters) and contact the factory before running the system.

Third, the system will test the contents of the nonvolatile memory. If it is OK the stored manifold volume will be displayed and the system will continue initialization. If there is an error in the nonvolatile memory, the manifold volume must be entered from the keyboard. A recalibration must be performed to store the manifold volume in the nonvolatile memory. User-specified analyses may be saved but a previously saved analysis may not be properly stored. The system may still be run normally.

APPENDIX 5

KRYPTON/MICROPORE OPERATIONS

A. VACUUM SYSTEM

When the AUTOSORB is supplied with the krypton/micropore option, a turbo pump is installed. This pump runs at all times the Autosorb is powered ON. The pump requires minimal maintenance.

When a turbo pump is installed, the front panel has an additional green LED below the DEWAR BATH STATIONS status display, plus a black reset button. The TURBO PUMP status is GOOD when this additional LED is NOT LIT. If this green LED is LIT, the TURBO PUMP is OFF. Press the reset button next to this LED to RESTART the turbo pump.

If the Autosorb has been turned off for a period of time, the manifold should be thoroughly evacuated before using the instrument. This is best accomplished by using the manual mode.

B. KRYPTON ANALYSIS PARAMETERS

When using the krypton option the MAXI-DOSE routine should not be employed. The dosing volumes required with krypton are sufficiently small that the increases provided with the MAXI-DOSE routine cause a risk of overshooting.

The saturated equilibrium vapor pressure, P_0, for krypton is usually taken as 2.63 mm Hg at the temperature of liquid nitrogen at standard pressure. This is the value which corresponds to the vapor pressure of the supercooled liquid state of krypton. You can obtain the saturated vapor pressure of krypton in any of the following ways when you complete the ANALYSIS PARAMETERS setup:

1. Enter it manually via the keyboard.

2. Instruct the AUTOSORB to use the P_0 station. This normally solidifies krypton in the P_0 cell and measures the equilibrium vapor pressure of *solid krypton*. Not recommended since most workers normally use P_0 corresponding to supercooled liquid (2.63 mm Hg).

3. Remove the P_0 cell from its station and select OPEN TO AMBIENT option. This causes the AUTOSORB to measure ambient pressure and to use the equations below to calculate the (liquid) P_0.

4. Select CALCULATED VALUE and enter ambient pressure (in mm of Hg). The Autosorb will calculate the equilibrium vapor pressure of supercooled liquid krypton from the equations given below.

The equation referred to above, the Clausius-Clapeyron Equation, is:

$$\ln \frac{P_a}{760} = \frac{\Delta H_v}{R} \left[\frac{1}{77.4} - \frac{1}{T} \right]$$

Where ΔH_v is the heat of vaporization of liquid nitrogen and P_a represents the local barometric pressure in mm of mercury.

This equation is used to calculate the bath temperature from ambient pressure assuming the heat of vaporization of liquid nitrogen is 1330 cal mol^{-1}.

From the calculated bath temperature the saturated equilibrium vapor pressure of supercooled liquid krypton is calculated from:

$$\log P_0 = -899.979 (1/T) - 12.55400 \log T + 34.38392 + 0.0175105 T$$

C. MICROPORE MEASUREMENTS. RECOMMENDATIONS AND PRECAUTIONS:

1. To obtain equilibrated isotherms in the micropore analysis it is recommended use Tolerance 0 and Equilibration time of 4 minutes or more.

2. To reduce time of such analysis it is recommended to use large bulb cell.

3. MAXIDOSE and INITIAL FILL should NOT be used for micropore measurements.

APPENDIX 6

THERMISTOR FINE TUNING

This procedure is used to calibrate the thermistor (either liquid nitrogen or liquid argon) to the sensor electronic LN_2 board. You will need a digital voltmeter and a small flat screwdriver. Read over these instructions carefully and contact Quantachrome if you have any questions before proceeding.

Procedure:

1. Remove the left side panel (facing front of AUTOSORB) of the instrument using a flat screwdriver. It is recommended to use plastic or insulated screwdriver so that accidentally dropping of the screwdriver will not cause any damage to the instrument circuits.

2. Connect the thermistor to the instrument. Fill a Dewar with liquid nitrogen to calibrate a LN_2 thermistor or liquid argon to calibrate a LAr thermistor. Place the filled Dewar on the Dewar drive.

3. Locate the **LN_2 board # 1** (For **AS-6**) inside the instrument. Use pictures / diagrams below as a guide in locating it. For **AS-3** calibrate the **LN_2 board # 2** first.

4. Open Manual Mode in the ASMWIN software. First, click the **Close All Valves** button. Next, click the **Dewar Drive** button to raise the dewar.

5. Connect the common terminal of the voltmeter to T0 (black). Connect the + (positive) terminal to T11 (blue). Measure and record the thermistor cold voltage. This value should be approximately **2.875 V** (DEWAR UP VOLTAGE).

6. Click **Dewar Drive** button to lower the dewar. Connect the + terminal to **T12 (Channel 1, Thermistor 1,** yellow). Adjust R12 using a flat screwdriver to adjust the reference warm voltage 100 mV (± 5 mV) below the thermistor cold voltage. Turning the screw of R12 counter-clockwise increases the voltage. Record the final reference warm voltage.

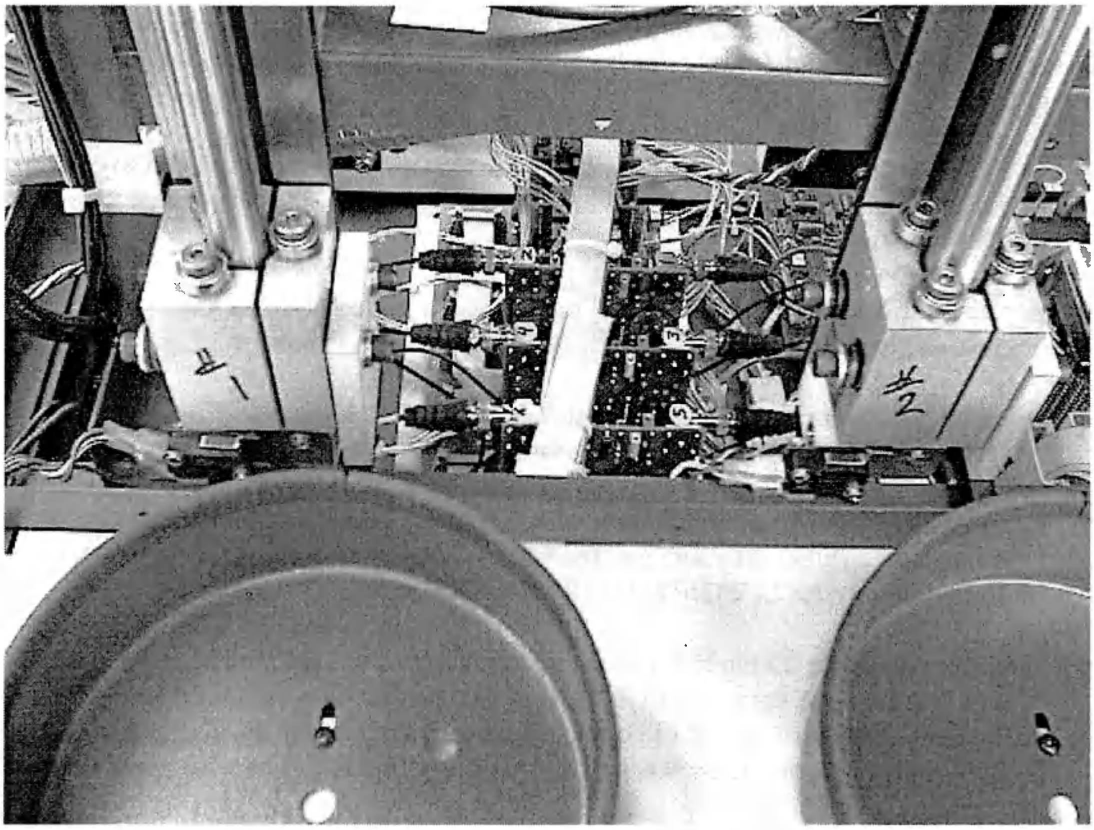
7. Connect the common terminal of the voltmeter to T0 (black). Connect the + (positive) terminal to T21 (blue). Measure and record the thermistor cold voltage. This value should be approximately **2.875 V** (DEWAR UP VOLTAGE).

8 Click **Dewar Drive** button to lower the dewar. Connect the + terminal to **T22 (Channel 2, Thermistor 2**, yellow). Adjust R22 using a flat screwdriver to adjust the reference voltage 100 mV (± 5 mV) below the thermistor cold voltage. Turning the screw of R22 counter-clockwise increases the voltage. Record the final reference warm voltage.

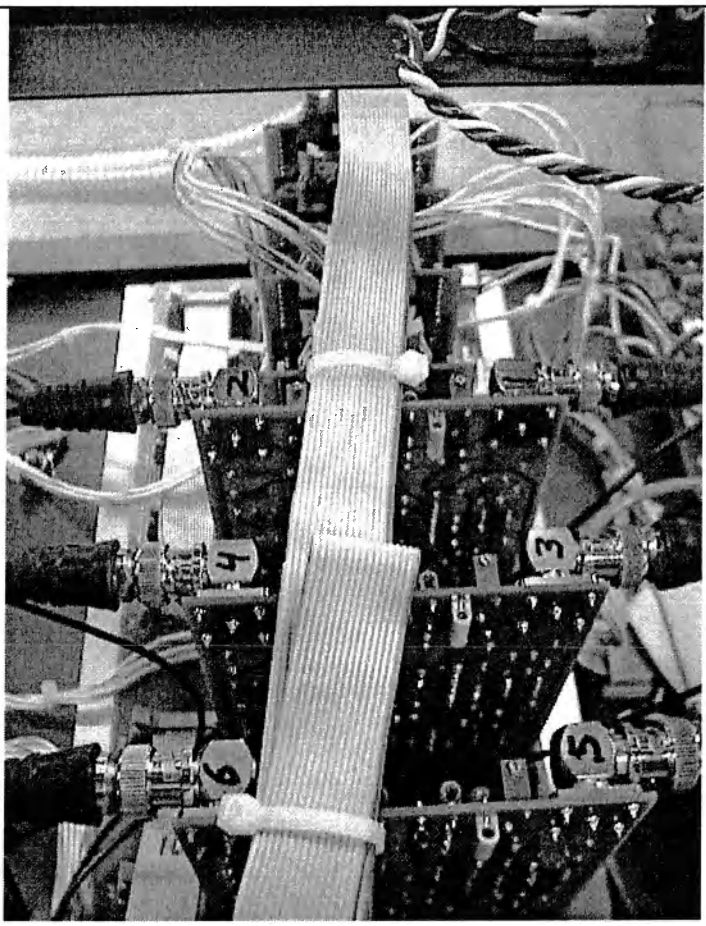
9 Follow the above procedure to adjust **LN_2 board # 2 & 3** for **Thermistor 3, 4, 5 & 6.** (For **AS-3** adjust **LN_2 board # 1** for **Thermistor 3,** See **Figure 1**)

10 Click the **Close All Valves** button and exit Manual Mode. Disconnect the terminals and replace the side panel.

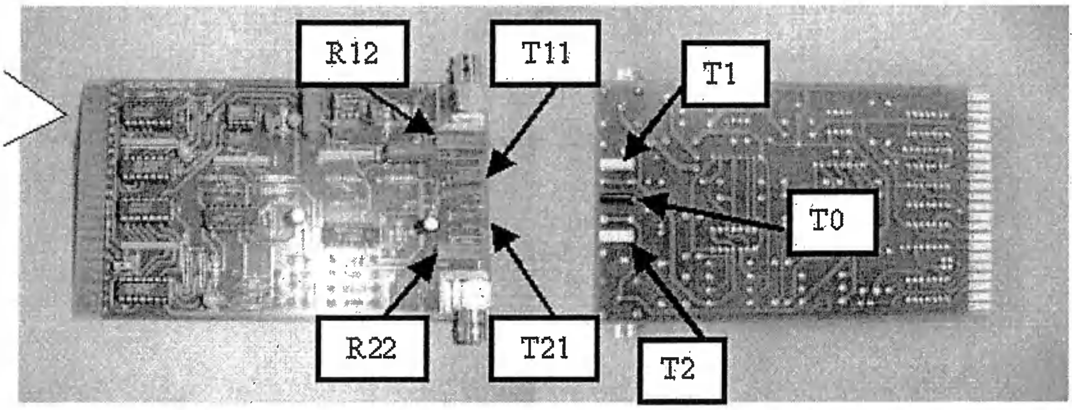
Note: AS-3 uses only two LN2 boards and the Thermistors are marked accordingly. For AS-3 you only have to Calibrate Thermistors 1, 2, 3.



Open Left Side panel (facing front of the AUTOSORB).



Channels are marked on each individual LN2 PCB



Indicates test points and potentiometers required to calibrate the LN2 PCB

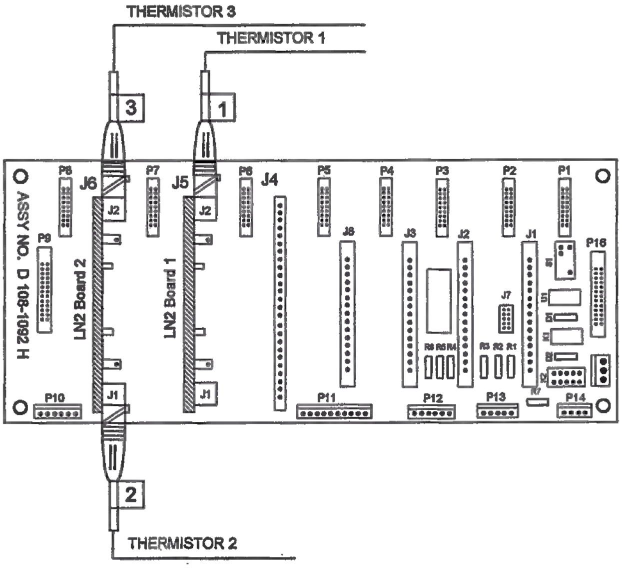


FIGURE 1 (AS-3)

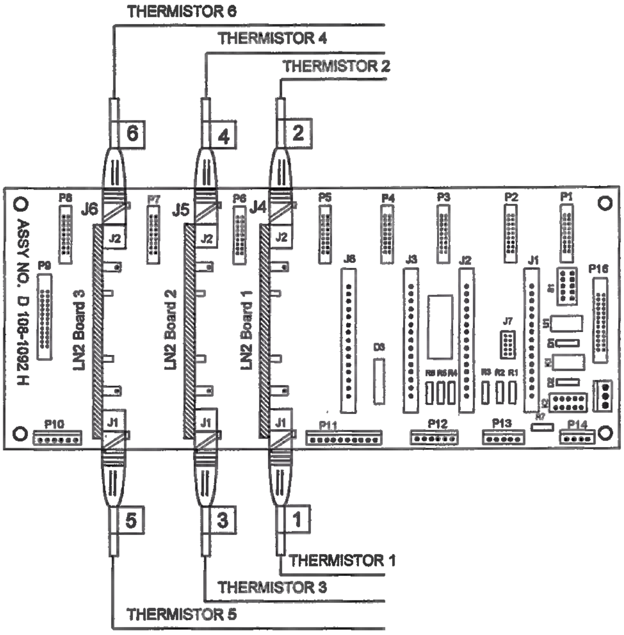


FIGURE 2 (AS-6)

For AS-3:

	Thermistor 2 (std bus **J6**)	**Thermistor 3** (std bus **J6**)
LN2 Ctrl. Board 2	BNC J1, Adjust R12	BNC J2, Adjust R22
DVM	Com(-):**T0** & Pos(+): **T12**	Com(-):**T0** & Pos(+): **T22**

	Thermistor 1 (std bus **J5**)	
LN2 Ctrl. Board 1	BNC J2, Adjust R22	
DVM	Com(-):**T0** & Pos(+): **T22**	

For AS-6:

	Thermistor 1 (std bus **J4**)	**Thermistor 2** (std bus **J4**)
LN2 Ctrl. Board 1	BNC J1, Adjust R12	BNC J2, Adjust R22
DVM	Com(-):**T0** & Pos(+): **T12**	Com(-):**T0** & Pos(+): **T22**

	Thermistor 3 (std bus **J5**)	**Thermistor 4** (std bus **J5**)
LN2 Ctrl. Board 2	BNC J1, Adjust R12	BNC J2, Adjust R22
DVM	Com(-):**T0** & Pos(+): **T12**	Com(-):**T0** & Pos(+): **T22**

	Thermistor 5 (std bus **J6**)	**Thermistor 6** (std bus **J6**)
LN2 Ctrl. Board 3	BNC J1, Adjust R12	BNC J2, Adjust R22
DVM	Com(-):**T0** & Pos(+): **T12**	Com(-):**T0** & Pos(+): **T22**

THERMISTOR COLD	**2.875 V** (Nominal)	**2.875 V** (Nominal)
THERMISTOR WARM	Thermistor cold – 0.100 ± 5 mV	Thermistor cold – 0.100 ± 5 mV

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