BELSORP

High Precision - Specific Surface Area / Pore Size Distribution Measuring Unit

Instruction Manual

Ver. 1. 3. 3

BELSORP-max

BELSORP series

【 Content 】

Cautions

1. BEL JAPAN, INC. reserves all rights to this instruction manual and to the software contained herein.
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3. All the information contained in this instruction manual and the software specifications are subject to change without notice.
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6. Please store the system disk carefully.
7. We are not liable for any damages resulting from improper use of this product.
8. The warranty term for **BELSORP-max** shall be for one (1) year after delivery.
9. Although this manual has been prepared with every precaution to ensure accuracy, please contact our company if you find any questionable points, errors, omissions, etc. in this manual.
10. Product(s) (including parts, technical data or information thereto) described in this manual shall be subject to export control laws and regulations of Japan or the US. You need to obtain the approval from appropriate government (s9 when you export if such laws ant regulations require.

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For safety use

Thank you very much for selecting **BELSORP-max.**

This manual describes safety precautions, instrument installation, sample measurement, etc., of which users should be aware before using this product.

Read through this instruction manual before you attempt using **BELSORP-max.**

After you read this manual, please keep it so as to be available at any time.

Precautions

For safety use, various precautions are described throughout this instruction manual. Thoroughly understand the precautions first, and then read the text. Be sure to follow the precautions.

To prevent any accident, the precautions that require your special attention are highlighted with a frame as shown on the right.

Indication level of severity

Warning	**Hazardous or unsafe practice that could result in severe injury or dead.**
Caution	**Hazardous or unsafe practice that could result in minor injury, or equipment and/or material could be damaged.**

Warning symbol

Symbol	**Caution (attention) is required.**
Symbol	**Prohibited (never do) .**
Symbol	**Enforced (must do) .**

Warning

Turn off power and disconnect the power plug in the event of any smoke, abnormal smell, or noise.

- **Using with abnormal conditions may result in fire and/or electric shock. Please contact our company.**

Turn off power and disconnect the power plug in the event of spilling water in the instrument.

- **Using the instrument with water spilled may result in fire and/or electric shock. Please contact our company.**

Install the instrument in a flat place with less vibrations, and take appropriate measures to prevent from falling down.

Use single phase AC power indicated on the back of the instrument, and be sure to install a grounding conductor.

Do not damage the power cable.

- **It may result in electric shock and/or failure of the instrument.**

Do not remove the rear panel.

- **There are rotating parts including a fan, and electric-charged parts in the instrument; therefore, touching directly these parts may result in injury and/or electric shock.**

Caution

Fix the power cable firmly so that it is not disconnected.

- **A plug is liable to generate heat. It may cause fire.**
- **The cable own weight applies a tension to the connections; therefore, be sure to fix it firmly.**

Use the instrument in a place with less electric noises.

- **Electric noise may cause improper operation.**

Please request us internal cleaning, when dust is accumulated inside the instrument.

- **It may result in fire and/or failure of the instrument.**

Do not install the instrument in a place with high temperature and humidity.

- **Use the instrument in a place having a temperature of 10 to 35 °C, and humidity of 20 to 80 %.**

Specifications

Measurement method	Volmetric gas adsorption method＋AFSM^{TM}	
Adsorptive	N_2, Ar, Kr, H_2, CO, O_2, CH_4, and other non-corrosive gas Steam (A corrosion resistant option is required for adsorption measurement of corrosive gas such as NH_3 and amine, and organic vapor such as CH_3OH, C_6H_6, etc.)	
Number of samples to be measured	Standard mode ($P/P_0 = 10^{-8}$ to 0.997): 1 to 3 samples High precision mode ($P/P_0 = 10^{-8}$ to 0.997): 1 to 2 samples (according to AFSM^{TM})	
Specific surface area measurement range [1)]	0.01 $m^2 g^{-1}$ or more (N_2 / 77K) 0.0005 $m^2 g^{-1}$ or more (Kr / 77K)	
Pore size distribution (diameter)	0.35 to 500 nm	
Pressure sensor	133 kPa	5 units (Accuracy: ±0.25 % of F.S.)
	1.33 kPa	2 units (Accuracy: ±0.5 % of R.)（OP. + 1 unit）
	13.3 Pa	1 unit (Accuracy: ±0.15% of R.)（OP. + 1 unit）
Pressure resolution	1.6×10^{-6} Pa	
manifold temperature	40 °C (Option 50 °C)	
Dewar vessel	Volume: 2.6 L　　Holding time: 60 h	
Sample cell	About 1.8 cm^3 (Option: 5 cm^3)	
Exhaust system	Turbo molecular pump + Rotary pump : Attainable vacuum: 6.7×10^{-7} Pa or less (manufacturer's specification) (Option: Oil free exhaust system)	
Vacuum gauge	Cold cathode gauge (2×10^{-7} pa to 1 Pa)	
Measurement program	Pretreatment and adsorption/desorption isotherm measurement	
Analysis program (BELMaster^{TM})	・ Adsorption /desorption isotherm ・ Specific surface area by Langmuir method ・ Pore volume calculation by DA method ・ Micro-pore analysis by MP method, HK method, and SF method ・ Difference of adosorption method ・ Specific surface area by BET method ・ Meso-Pore analysis by DH method, CI method, BJH method ・ Micro-pore volume and micro-pore diamether by t-method, α_s method ・ Equivalence diffential adsorption heat analysis ・ Pore size distribution analysis by the NLDFT/GCMC (BELSim^{TM}) (Optional)	
Required PC environment	OS: Windows 2000, XP, Vista, 7　　CPU: Intel Processor Memory: 2 GB or more　　Hard disc: Free spaces of 1 GB or more USB port: USB 2.0	
Auxiliary equipment	Rotary pump displacement: 50 L min^{-1}　　Attainable vacuum: 6.7×10^{-2} Pa	

Utility	He, absorptive (N_2, Ar, etc.) : 1/8” Swage lock joint (0.1MPa (G)) Air for valve operation : 1/4” Plastics tube quick connect (0.5 to 0.6MPa (G)) Rotary pump connection port : OD ϕ11 mm Hose nipple
Dimension / weight	W565 x H850 x D580 mm, 84 kg (Excluding a vacuum pump and computer related equipment)
Power	Single phase, AC100 to 120 V or AC200 to 240 V /800 VA (max. 700VA for roughing vacuum pump)

1) The minimum measurable specific surface area depends on the sample density.

Optional equipment specifications

Temperature controller	Power	Single phase, AC100 to 240 V / 600 VA	
	Dimension / weight	W145 x H200 x xD300 mm, 4 kg	
450 °C heater	Number of ports	3	
	Temperature range	50 to 450 °C	
	Temperature stability	±0.2 °C	
	Overheat detection temperature	500 °C	
	Temperature control	PID control using a temperature controller in the temperature device controller	
	Dimension / weight	W280 x H240 x D270mm, 6.5 kg	
550 °C heater	Number of ports	3	
	Temperature range	50 to 550 °C	
	Temperature stability	±0.5 °C	
	Overheat detection temperature	600 °C	
	Temperature control	PID control using a temperature controller in the temperature device controller	
	Dimension / weight	W280 x H240 x D270 mm, 9 kg	
1100 °C electric furnace	Number of ports	1	
	Temperature range	50 to 1100 °C	
	Temperature stability	±0.5 °C	
	Overheat detection temperature	1150 °C	
	Temperature control	PID control using a temperature controller in the temperature device controller	
	Dimension / weight	W280 x H300 x D270 mm, 6 kg	
Water bath	Operating temperature range	-10 °C to 70 °C	
	Wetted material	SUS304, SUS410, silicon rubber	
	Dimension	W280 x H240 x D270 mm	
	Weight	Open system	6 kg
		Closed system	6 kg
	Volume	Open system	2.1 L
		Closed system	Internal bath: 0.7 L
			External bath: 1.4 L
	Joint	OD. ϕ13 mm hose nipple	

Gas selector	Number of ports	4
	Gas connection port	1/8” swage lock joint (0.5 to 1.5 bar)
⚠ In case of using corossive gas, use the specially designed port V2 or V3.		
Flow gas pretreatment line	Connected to the unit using a flow gas sample cell	
Corrosion resistant exhaust system	Rotary pump (Fonbrin oil type) : Displacement: 30 L min^{-1} Attainable vacuum: 200 Pa	
Oil free exhaust system	Diaphragm pump: Displacement : 15 L min^{-1} Attainable vacuum: 350 Pa	
	Corrosion resistant diaphragm pump: Displacement: 20 L min^{-1} Attainable vacuum: 200 Pa	

Before measuring samples

About BELSORP-max

The gas adsorption method is one of the important experimental means for characterizing fine particles or porous materials. However, operation of the conventional adsorbing device was complicated, and a skilled person was required to obtain the measurement data accurately. BELSORP-max, an automatic gas adsorption measuring unit for gas adsorption, vapor adsorption and chemisorption, is designed to measure accurately, quickly the properties of fine particles, such as the specific surface area, pore size distribution and metal dispersion, by easy operation using the gas adsorption method.

1. Various measurement items

Various items, such as the specific surface area, pore size distribution and metal dispersion, can be measured using a single measuring unit, by applying gas adsorption, vapor adsorption, and chemisorption.

2. A wide range of adsorption isotherm

The adsorption isotherm can be measured in the range from $P/P_0 = 10^{-8}$ to 0.997.

3. Vapor adsorption as standard unit

The vapor adsorption measurement is included as standard equipment.

4. Measurement system without refrigerant control (AFSM™)

The refrigerant level control is not required for the unique dead volume measurement system. This eliminates troubles related to the level control, and enables highly repeatable measurement.

5. Automatic measurement of the saturation vapor pressure

In the nitrogen adsorption measurement at liquid nitrogen temperature and the argon adsorption measurement at liquid argon temperature, the saturation vapor pressure is influenced largely from atmospheric pressures, and the measured data especially around the relative pressure of 1.0 have a large error. **BELSORP-max** eliminates the error caused from the saturation vapor pressure change, by measuring simultaneously the saturation vapor pressure of nitrogen and argon using the specially designed port (P0 port).

6. Automatic measurement of the adsorption/desorption isotherm and the metal dispersion

Various own-developed software applications offer high operability. Once the sample cell is set, the subsequent measuring processes are performed automatically. The measured data are analyzed using a variety of software applications, and then output to a display or a printer. Moreover, the instrument can be diagnosed by running the system check software application.

7. Multi-gas applicability

Nitrogen, argon, krypton, steam, and other adsorptive gas (except corrosive gas) can be measured for the respective adsorption isotherms. The optional gas selector enables seven different types of gas to be connected at a time.

8. Measuring up to 3 samples in parallel

Each measurement port is equipped with pressure sensors; and measuring up to 3 samples can be

performed in parallel.

9. Automatic measurement with 8 measuring units

A PC controls up to 8 units of BELSORP-max.

10. Compact and economy

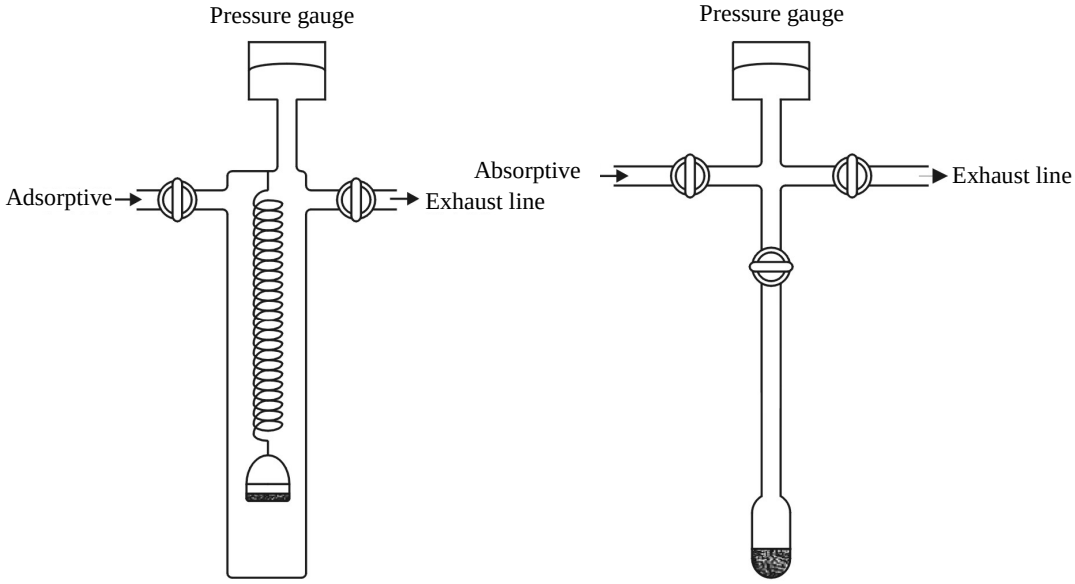
The streamlined design enabled a compact instrument, and offers at a low cost.

The general principle of gas adsorption method, and measurement system of BELSORP-max

ooo Volumetric and gravimetric gas adsorption method ooo

1. General Principle

Among various adsorption measurement methods, the gravimetric and the volumetric gas adsorption method are extensively used (Fig. 1).



Gravimetric gas adsorption method　　Volumetric gas adsorption method

Fig. 1

The gravimetric gas adsorption method is relatively simple in terms of the measurement principle and the experiment method; therefore, it has been extensively used as the adsorption isotherm measurement method. As to the gravimetric gas adsorption method, however, a skillful technique is required for a stable operation of a highly sensitive microbalance, and it is difficult to measure accurately a small weight change by adsorption. Furthermore, the gravimetric gas adosorption method in which the sample is hung down requires verifying whether the sample temperature has reached the adsorption temperature, and also whether it has reached the heat equilibrium since adsorption heat is generated. For the reasons mentioned above, the gravimetric gas adosorption requires a highly skilled technique for obtaining the adsorption data accurately.

As to the volumetaric gas adsorption, on the other hand, it reaches the heat equilibrium quickly before and after the adsorption process. With the volumetaric gas adsorption method, the measurement system volume is measured precisely to determine the adsorption. Then, the adsorption is calculated from the gas pressure change in the measurement system, using the equation of state for gas. Moreover, the sample handling is much easier than those by the gravimetric gas adsorption method.

2. Measurement system of BELSORP-max

BELSORP-max is a full automatic gas-adsorption measuring unit, which adopts the constant volume method for the measurement system. The reference volume buffer and each measurement port are equipped with pressure sensor, all of which enable higher accuracy measurement. Highly repeatable data can be obtained by easy operation.

ooo Pretreatment ooo

1. Principle

The gas adsorption measurement process includes; sample pretreatment, dead volume measurement, adsorption measurement, and then desorption measurement.

Solid surfaces are sensitively influenced by environment. Samples with a larger specific surface area are influenced more strongly. In the pretreatment, appropriate environments shall be provided according to the measurement intended, and it shall not change any properties on the sample surface.

The gas adsorption measurement determines the adsorption per 1g-sample. When the error in mass is as large as 1 %, the measurement accuracy is influenced by the error to the same extent. Therefore, it is required to accurately determine the sample weight from the blank sample cell weight and the sample cell weight after pretreatment.

In order to measure the adsorption isotherm accurately, it is important to perform the pretreatment with suitable conditions. The pretreatment shall be performed on such conditions as the gas and moisture adsorbed surface can be removed without denaturalizing the sample. The sample mass shall be obtained accurately. The pretreatment methods include the vacuum heating treatment, the flow gas heating treatment, etc.

2. Pretreatment with BELSORP-max

Pretreatment with **BELSORP-max** can be performed while vacuuming at room temperature. **The optional heater and electric furnace** enables the vacuum heating pretreatment, whereas the flow gas pretreatment line enables the flow gas pretreatment.

⚠ **When volatile vapor or gas are generated by heating samples, it may contaminate the instrument. Pre-treat or dry samples with BELPREP-vac II, BELPREP-flow II, or other pretreatment devices before the pretreatment with BELSORP-max.**

ooo Dead volume measurement ooo

1. General Principle

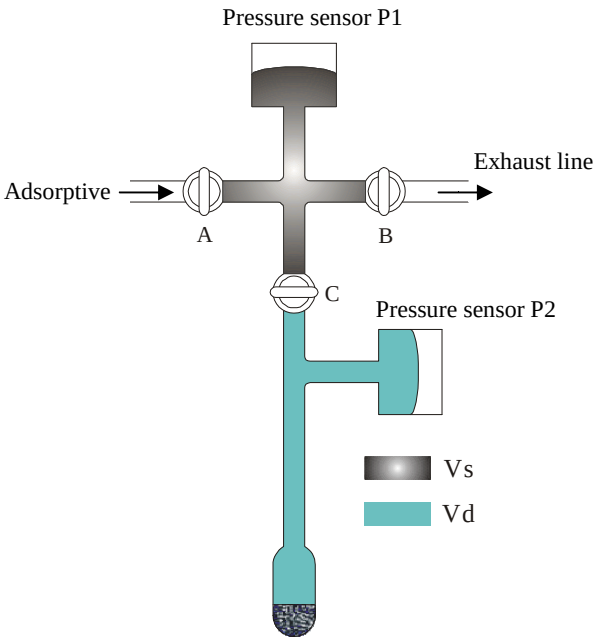


Fig. 2

The space volume in the sample cell is called " Dead Volume (*Vd*) " (Fig. 2).

When the sample cell and the amount of samples change, naturally the *Vd* value changes. Therefore, *Vd* has to be measured for every adsorption measurement. Here, *Vd* is determined as follows.

Install the sample cell to the adsorbing device after pretreatment, and then exhaust the measurement system. Keep the sample temperature at constant. Dose helium gas into the reference volume buffer *Vs*, and measure the pressure $P1_i$ *(1)* using the pressure sensor P1. The reference volume buffer *Vs* has been calibrated, and is specific to each instrument. Open the valve C between *Vd* and *Vs* to diffuse helium gas in the space of *Vd*, and then close the valve C several seconds later. Now, $P1_e$ *(1)* represents the pressure at the pressure sensor P1, while $P2_e$ *(1)* represents the pressure at the pressure sensor P2. With an assumption that the helium gas adsorption to the sample and/or the wall could be negligible, the first point dead volume *Vd (1)* can be determined using the following equation.

$$Vd(1) = \frac{\left(P1_i(1) - P1_e(1)\right) \times Vs}{P2_e(1)}$$

Then, dose additional helium gas, and measure the pressure $P1_i$ *(2)* with the pressure sensor. Diffuse helium gas into the space of *Vd* using the same procedure as for the first point. Now, $P1_e$ *(2)* represents the pressure at the pressure sensor P1, while $P2_e$ *(2)* represents the pressure at the pressure sensor P2. The second point dead volume *Vd (2)* can be determined as the following equation.

$$Vd(2) = \frac{\left(P1_i(2) - P1_e(2)\right) \times Vs + P2_e(1) \times Vd(1)}{P2_e(2)}$$

In the same manner, the *n*-th point dead volume can be expressed as follow.

$$Vd(n) = \frac{\left(P1_i(n) - P1_e(n)\right) \times Vs + P2_e(n-1) \times Vd(n-1)}{P2_e(n)}$$

2. Dead volume measurement system with BELSORP-max (AFSM™)

In the nitrogen adsorption measurement, the sample section is refrigerated with liquid nitrogen to keep the adsorption temperature in the sample section constant. The dead volume (*Vd*) changes as the liquid nitrogen level changes. Generally, the liquid nitrogen level is controlled as to be constant, and the dead volume is fixed.

BELSORP-max uses a new dead volume measurement system (Advanced Free Space Measurement) that does not require the liquid nitrogen level control, and accordingly it offers a compact design, low cost, and high operability. Liquid nitrogen is filled in the Dewar vessel (about 2.6 L) for cooling samples before measurement. The liquid nitrogen in the Dewar vessel vaporizes during the adsorption measurement of samples, and it decreases gradually (it retains for 60 hours or more). The dead volume in the sample cell changes gradually along with this level drop. **BELSORP-max** measures the changing dead volume as follows. A dead volume reference cell (blank sample cell: the same as the sample cell used for measurement) is soaked in liquid nitrogen together with the sample cell (Fig. 3). Prior to the adsorption measurement, the dead volume in the sample cell is measured, as well as those in the dead volume reference cell. Now, the liquid nitrogen level is at level 1 as shown in Fig. 3. $Vd_{(smp)}(1)$ represents the dead volume of the sample cell, while $Vd_{(ref)}(1)$ and $P_{(ref)}(1)$ represent the dead volume of the reference cell and the pressure, respectively. $P_{(ref)}(2)$ represents the pressure in the dead volume reference cell when the liquid nitrogen level drops to level 2. Then, the dead volume of the reference cell $Vd_{(ref)}(2)$ and the difference $\Delta Vd_{(ref)}$ at level 2 are expressed as follow.

$$Vd_{(ref)}(2) = Vd_{(ref)}(1) \times P_{(ref)}(1) / P_{(ref)}(2)$$

$$\Delta Vd_{(ref)} = Vd_{(ref)}(2) - Vd_{(ref)}(1)$$

Since the dead volume change in the sample cell is equal to those in the dead volume reference cell ($\Delta Vd_{(smp)} = \Delta Vd_{(ref)}$, within ± 0.2 % based on our data), the dead volume, $Vd_{(smp)}(2)$, of the sample cell at level 2 can be expressed as follow.

$$Vd_{(smp)}(2) = Vd_{(smp)}(1) + \Delta Vd_{(smp)}$$

$$= Vd_{(smp)}(1) + \Delta Vd_{(ref)}$$

In such a way, highly reliable data can be obtained by measuring the dead volume at each measuring point.

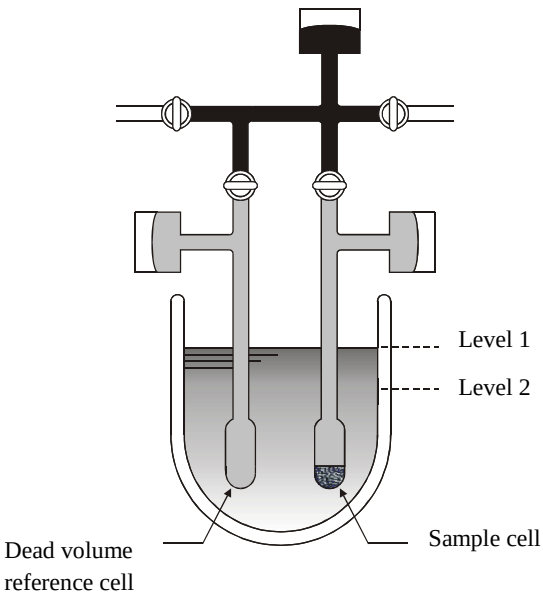


Fig. 3

ooo Adsorption measurement and desorption measurement ooo

1. The generally principle of adsorption measurement

The adsorptive gas pressure dosed to the sample cell from the reference volume buffer *Vs* decreases due to adsorption. In the volumetric method, the amount of adsorption is determined from this pressure difference before and after the adsorption.

Now, $P1_i(n)$ (kPa) represents the adsorptive pressure dosed to *Vs* through the valve-A, as shown in Fig.2 on page 15, at the *n*-th point adsorption measurement. Also, $P1_e(n)$ represents the pressure at the pressure sensor P1, and $P2_e(n)$ represents the pressure at the pressure sensor P2 while reaching the adsorption equilibrium by opening the valve C; the *n*-th point adsorption $V(n)$ (amount of adsorption per 1g-adsorbent being converted into the gas volume in a standard state) can be determined using the equation of state for ideal gas, as follow.

Firstly, the gas volume *V1* in *Vs* (cm^3 (standard state) / g^{-1}), which changed before and after the adsorption, is expressed as the following equation. *Ws* and *T* are the sample weight and the absolute temperature of *Vs*, respectively.

$$V1 = \frac{\left(P1_i(n) - P1_e(n)\right) \times Vs \times 273.15}{101.30 \cdot Ws \cdot T}$$

The gas volume *V2* in *Vd*, which changed before and after adsorption, can be determined from the (*n*-1)-th point equilibrium pressure $P2_e(n\text{-}1)$ in *Vd*, and the *n*-th point equilibrium pressure $P2_e(n)$ in *Vd*, as follow.

$$V2 = \frac{\{P2_e(n-1) - P2_e(n)\} \times Vd \times 273.15}{101.30 \cdot Ws \cdot T}$$

The sample's adsorption change ΔV in the *n*-th point's adsorption process is equal to the gas volume in *Vs* and *Vd* that changed before and after adsorption; therefore it is expressed with the following equation.

$$\Delta V = V1 + V2$$

Hence, the adsorption $V(n)$ at the adsorption equilibrium pressure $P2_e(n)$ is expressed as follow.

$$V(n) = V(n-1) + \Delta V$$

2. The general of principle desorption measurement

The desorption isotherm is measured as follows. Now, $P1_i(n)$ (kPa) represents the adsorptive pressure when *Vs* is depressurized through the valve B while closing the valve C, shown in Fig.2 on page 15, at the n-th point desorption measurement. Also, $P1_e(n)$ represents the pressure at the pressure sensor P1, and $P2_e(n)$ represents the pressure at the pressure sensor P2 while reaching the adsorption equilibrium by opening the valve C. Then, the *n*-th point's adsorption $V(n)$ can be determined using the same equation as for the adsorption process.

ooo Saturation vapor pressure measurement ooo

1. Principle

The nitrogen gas adsorption measurement at liquid nitrogen temperature is effective to determine the specific surface area and pore size distribution of samples. This measurement uses liquid nitrogen as refrigerant to cool samples. The liquid nitrogen boiling point changes as the atmospheric pressure changes, and accordingly the saturation vapor pressure of nitrogen changes. When a fixed value (e.g. atmospheric pressure = 101.3 kPa) is used for the saturation vapor pressure, highly repeatable data cannot be obtained especially in high relative pressure areas.

2. Saturation vapor pressure measurement system with BELSORP-max

BELSORP-max enables highly repeatable measurement in high relative pressure areas by measuring the saturation vapor pressure. The saturation vapor pressure value can be specified by the following two different modes.

1 Saturation vapor pressure measurement mode	This mode is selected for the nitrogen adsorption measurement at liquid nitrogen temperature, and the argon adsorption measurement at liquid argon temperature. The saturation vapor pressure is measured at each adsorption measurement point, by liquefying adsorptive gas at the P0 port, a specially designed port for the saturation vapor pressure measurement. Highly precise data can be obtained.
2 Input value mode	An input value is used to specify the saturation vapor pressure.

ooo Non-ideality correction of the adsorptive gas ooo

1. General principle

The relation between the gas pressure P, the molecular volume V_m, and the temperature T is expressed as:

$$PV_m = zRT$$

Where, z is referred to as compressibility factor, which is always 1 for the ideal gas. For the real gas, however, it deviates from the ideal gas to some extent. The compressibility factor z of nitrogen gas, for example, is 1.000 at pressure of 100 kPa or less, and temperature of 300 K, but it is 0.956 at pressure of 100 kPa, and temperature of 77 K. This means that the number of moles is about 4 % larger than those estimated for the equation of state of ideal gas when the nitrogen gas in a certain volume is refrigerated at liquid nitrogen temperature, and the pressure is around atmospheric pressure. Therefore, when calculating the adsorption by the volumetric method, it is necessary to correct the non-ideality to obtain a highly accurate result.

2. System of BELSORP-max

BELSORP-max corrects the non-ideality of nitrogen gas at liquid nitrogen temperature. When the dead volume Vd is divided into the real volume V_L that is put in liquid nitrogen and the real volume V_R at room temperature as shown in Fig. 4, the dead volume Vd is expressed as follow.

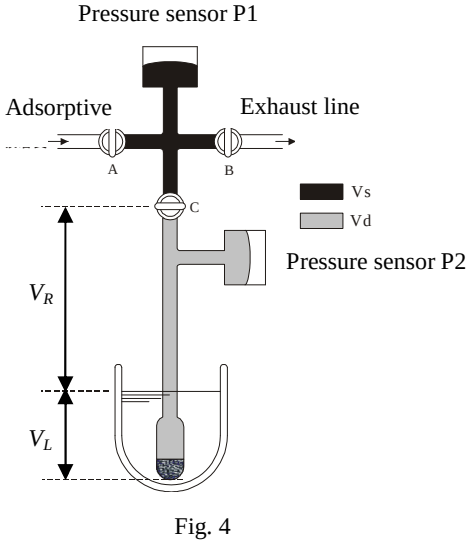


Fig. 4

$$Vd = V_R + V_L \frac{T_R}{77.35} \qquad (1)$$

Where, T_R represents room temperature. The correction of non-ideality at nitrogen adsorption / desorption measurement is applied to V_L. Using a compressibility factor z, the dead volume Vd' after correction is expressed as:

$$Vd' = V_R + V_L \frac{T_R}{77.35 \cdot z} \qquad (2)$$

Accordingly, the correction Δ added to the dead volume measured with helium is expressed as:

$$\Delta = Vd' - Vd = V_L \frac{T_R}{77.35}\left(\frac{1-z}{z}\right) \qquad (3)$$

Once V_L is determined, the dead volume after correction can be determined. Now, the dead volume at room temperature Vd_{RT} can be expressed:

$$Vd_{RT} = V_R + V_L \qquad (4)$$

Therefore, V_L can be determined by subtracting (4) from (1), as follow.

$$V_L = (Vd - Vd_{RT})\left(\frac{77.35}{T_R - 77.35}\right) \qquad (5)$$

The compressibility factor z is determined using the virial equation of state as follow.

$$z = 1 + \frac{B}{RT}P$$

Where, B represents the second virial coefficient, while P represents pressure.

ooo Correction of thermal transpiration ooo

1. General principle

When two vessels with different temperature are connected with a tube, the pressure in a vessel may differ from those in the other vessel. This effect is referred to as thermal transpiration. It may be significant when the pressure is 1 kPa or less, the tube diameter is several millimeters or less, and the temperature difference between the vessels is large.

2. System with BELSORP-max

BELSORP-max corrects the thermal transpiration using the following equation.

$$\frac{P_2}{p_1} = \frac{AX^2 + BX + C\sqrt{X} + \sqrt{(T_2/T_1)}}{AX^2 + BX + C\sqrt{X} + 1}$$

$$X = 7.50 \times 10^{-3} P_2 d$$

$$A = 1.4 \times 10^4 \exp(1.17 \times D \times 10 \times (T)^{-2}$$

$$B = 5.6 \exp(1.40 \times D \times 10) \times (T)^{-1}$$

$$C = ((1.10 \times 10 / D) - 14) \times (T)^{-0.5}$$

$$T = \frac{T_1 + T_2}{2}$$

P_1: Sample cell pressure (Pa)

P_2: Manifold pressure (Pa)

T_1: Sample cell temperature (K)

T_2: Manifold temperature (K)

d: Sample cell inner diameter (mm)

D: Molecular diameter (nm)

Nomenclature and function of individual components

ooo Main unit-front ooo

① Lifting switch

A manual switch to lift the Dewar vessel, water bath, heater, and electric furnace. It is usually controlled by a signal from a computer; however, it can be controlled manually where applicable.

▲: Lift-up button. Press this button for a short period to lift up. Hold depressing this button for 5 seconds to keep lifting up even after releasing it. It stops by pressing the stop button or when it lifts up to the upper limit position.

■: Stop button. It stops by pressing this button while lifting. It blinks when a protective function works due to overload while lifting. In such a case, press the **reset switch** in the temperature controller pocket ③.

▼: Lift-down button. Press this button for a short period to lift down. Hold depressing this button for 5 seconds to keep lifting down even after releasing it. It stops by pressing the stop button or when it lifts down to the lower limit position.

⚠ Do not press the lifting switch while measuring samples.
⚠ Do not put your hand or other materials on the temperature device while lifting.

② Power indicator

This indicates power switch to the instrument. It is interlocked with a power switch on the back of the instrument.

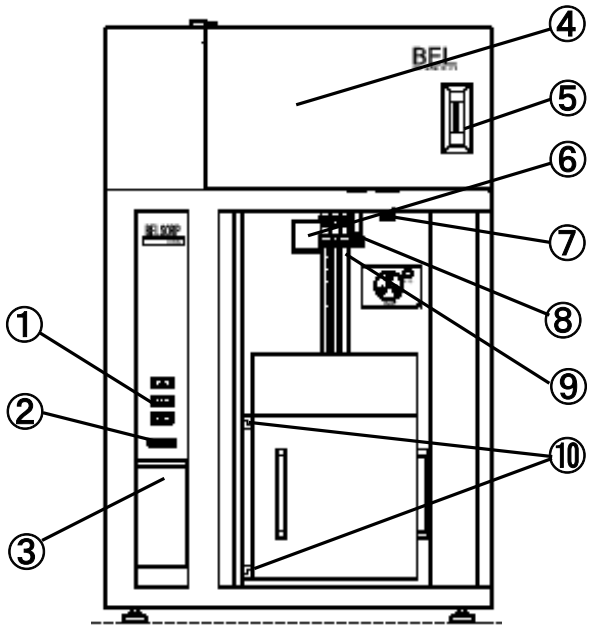
③ Temperature controller pocket

Pull the handle to open the pocket. The following devices are mounted in the pocket.

Temperature controller for the thermostatic chamber: A temperature controller used for the thermostatic chamber.

Reset button for the elevator: The lifting operation stops when the elevator is overloaded. In such a case, it is not recovered automatically even after removing the load. Press this reset switch to release the protection.

⚠ Do not change the temperature setting for the thermostatic air chamber temperature controller.
⚠ Pay careful attention to prevent your finger from being pinched while closing the pocket.



⑥ Needle valve adjustment screw storage shutter

The needle valve adjustment screw is located inside this shutter. Adjust the valve opening with this screw to control the gas flow. Viewing from the front of the main unit, the screw C (for a large flow rate) is on the left, while the screw F (for a small flow rate) is on the right.

⚠ Do not keep the shutter open, because the thermostatic chamber is connected to the shutter.

⑦ Adsorptive gas dosing port (ads. 2)

This is used as a gas connection port by mounting a liquid bottle and an accessory conversion connector.

⑧ Flow gas sample cell connection port

This port is for connecting the flow gas line only (when the optional “flow gas pretreatment line” is selected).

⑨ Measurement port and saturation vapor pressure measurement P0 port

A small tube in the middle is the saturation vapor pressure measurement P0 port, and the other 3 tubes are the measurement ports.

④ Head cover

This cover offers thermal insulation to the manifold temperature.

⑤ Flow meter

The flow rate at the flow gas pretreatment can be monitored (when the optional "flow gas pretreatment line" is selected).

⑩ Elevator hanger

Slide this to mount the temperature devices, such as the Dewar vessel, water bath, heater, electric furnace, etc. Be sure to slide it to the back limit, when mounting the device.

ooo Main unit-back side ooo

① Compressed air (gas) supply port

This is to operate the pneumatic valve for changing the internal flow circuit. Supply compressed air or inert gas of 0.5 to 0.6 MPa (gauge pressure).

② Helium gas supply port

Connect the helium gas line. Supply helium gas of 0.1 MPa (gauge pressure).
Connector: 1/8" swage lock

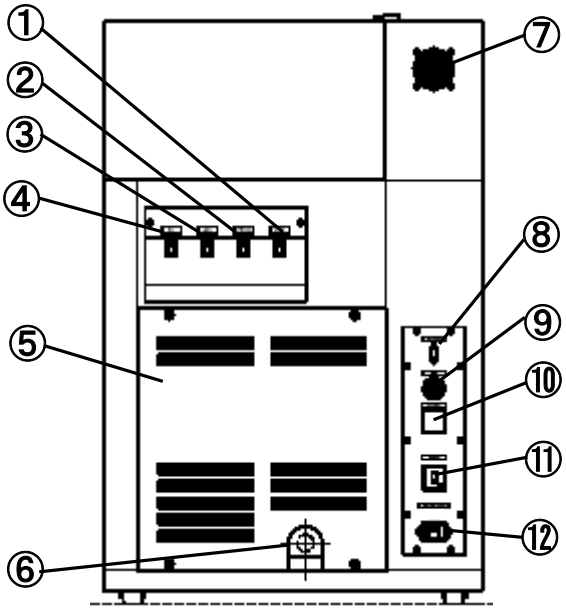
③ Adsorptive gas dosing port (Ads. 1)

Connect the adsorptive gas line. Supply adsorptive gas of 0.1 MPa (gauge pressure).
Connector: 1/8" swage lock

④ Vent connection port

This exhaust port is to discharge the used gas in the flow gas pretreatment. Connect a 1/8" tube, and install the other end to a well-ventilated place.
Connector: 1/8" swage lock

❗ It is dangerous to perform the flow gas pretreatment without the exhaust tube connected to the vent port, since the used gas is discharged. Be sure to install an exhaust line to the vent port when performing the flow gas pretreatment.



⑤ Back door latch lock

Remove this door when performing the turbo molecular pump maintenance. Turn the slot on the clip screw (at 4 locations each) to the vertical direction to remove the door. Turn the slot to the horizontal direction to secure the door.

⑥ Pump hose hole

Connect the roughing vacuum pump to the turbo molecular pump in the instrument with a hose by passing it through this hole.

⑨ USB communication connection port

USB male connector. This is to connect to the computer. Use a USB male (type A) and USB male (type B) cable to connect to the computer.

⑩V. P. AC

Connect the power cable to the rotary pump.

⚠ Be sure to connect the rotary pump power cable to this AC outlet.
⚠ Do not connect any equipment except the pump.

⑦ Cooling fan This fan cools inside the instrument. It is interlocked with a power switch on the back of the instrument.	**⑪POWER switch** Turns on / off the power to the main unit and roughing vacuum pomp.
⑧ Connection port of Temp. cntl. D-sub 9-pin, female connector. This is to connect to the optional temperature controller. Use a straight cable with D-sub 9 pin, male and D-sub 9 pin, female to connect to the temperature controller.	**⑫ Power inlet** Supply power to the main unit. Be sure to use the accessory IEC power cable.

ooo Main unit-left side ooo

① Solenoid valve access door

An access door for the solenoid valve to control pneumatic valve and the internal cooling fan.

② Gas supply port (Aux. 1 to 4)

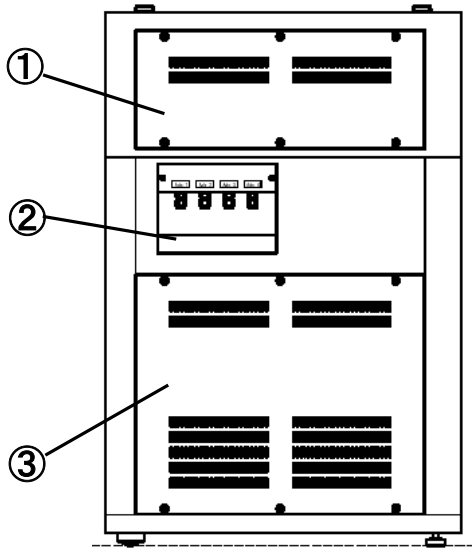
Connect the dosing gas line. Supply the dosing gas at pressure of 0.1 MPa (gauge pressure) (when the optional “gas selector” is selected).

⚠ In case of using corossive gas, use the specially designed port V2 or V3.

③ Control section access door

Electric control parts are located in the door.

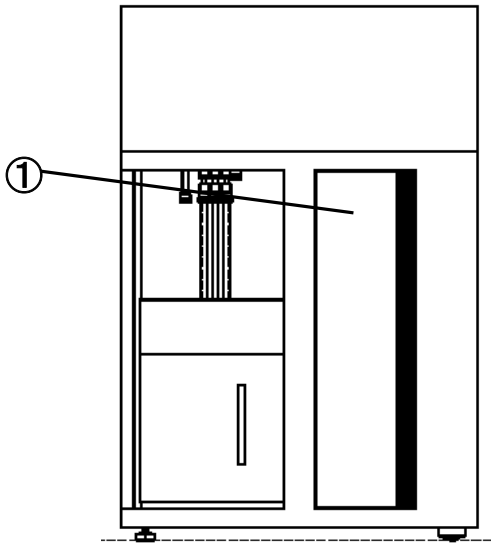
⚠ Some electric-charged parts are exposed inside the door. Except an engineer from our company, do not open this door. Otherwise, it may result in electric shock.



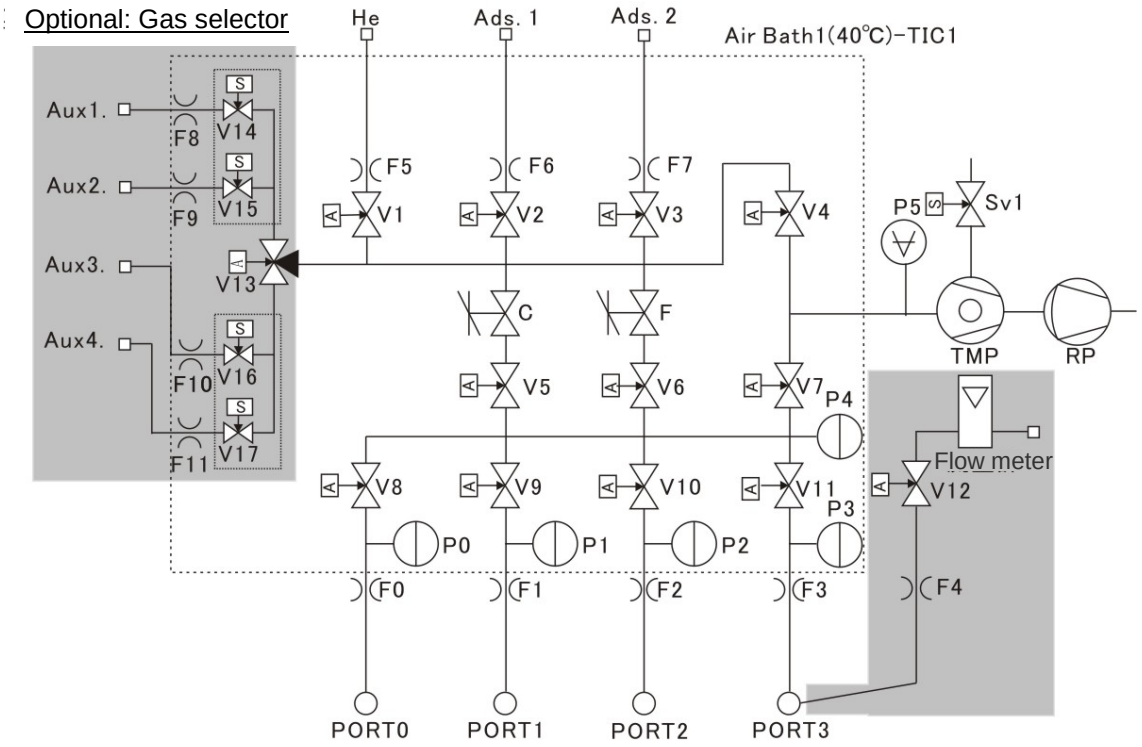
ooo Main unit-right side ooo

① Fan filter cleaning door

A filter is located in the door. This filter is for the cooling-fan of turbo molecular pump. Check periodically the filter and clean it up where applicable.



ooo Main unit-inside ooo



① V1 to V17 : Valve

② C, F : Flow rate adjustment needle valve

③ P0 to P4 : Pressure sensor

④ P5 : Vacuum gauge

⑤ TIC1 : Manifold temperature controller

⑥ Sv1 : Vent valve

⑦ TMP : Turbo molecular pump

① Valve (Standard unit: V1 to 11)

V1 to 11: pneumatic valves

V1 : To dose helium gas

V2 : To dose the Ads. 1 gas

V3 : To dose the Ads.2 gas or vapor

V4 : To exhaust the gas accumulator

V5 : To dose gas to the reference volume (a large flow rate line)

V6 : To dose gas to the reference volume (a small flow rate line)

V7 : To exhaust the reference volume

V8 : A valve between the P0 port and the reference volume

V9 : A valve between the measurement port 1 and the reference volume

V10 : A valve between the measurement port 2 and the reference volume

V11 : A valve between the measurement port 3 and the reference volume

Valve (optional)

Flow gas pretreatment line

A pneumatic valve

V12 : To be used in the flow gas pretreatment

Gas selector

V13: Pneumatic valves, V14 to V17: Solenoid valve

V13 : A valve between the gas selector and the gas accumulator

V14 : To dose the Aux. 1 gas

V15 : To dose the Aux. 2 gas

V16 : To dose the Aux. 3 gas

V17 : To dose the Aux. 4 gas

⚠ In case of using corossive gas use the specially designed port V2 or V3.

② Flow rate adjustment needle valve (C, F)

C : For a large flow rate (pressure) control

F : For a small flow rate (pressure) control

③ Pressure sensor (P0 to P4)

The following pressure gauges, with the indicated respective full scale, are installed to each port.

P0 : 133 kPa
To measure pressure at the saturation vapor pressure measurement port (P0 port)

P2 : 133 kPa
To measure pressure at the measurement port 2

P4 : 133 kPa, 1.33 kPa
To measure pressure in the reference volume

P1 : 133k Pa (Optional: 1.33 kPa, 0.0133kPa)
To measure pressure at the measurement port 1

P3 : 133 kPa, 1.33 kPa, 0.0133 kPa
To measure pressure at the measurement port 3

Accuracy: 133 kPa → ±0.25 % (full scale)
: 1.33 kPa → ±0.5 % (reading)
: 0.0133 kPa → ±0.15 % (reading)

④ Vacuum gauge (P5)

Pirani gauge + cold cathode type pressure sensor

Measurement range: 5 x 10^{-7} Pa to atmospheric pressure

⚠ Do not use the vacumue gauge at pressure of 0.1 Pa or more.

⑤ Manifold temperature controller (TIC1)

Turn on the power switch on the back of the main unit, then the thermostatic manifold temperature is controlled to be 40°C (Option 50 °C). The thermostatic manifold temperature is measured using a platinum temperature detector.

⑥ Vent valve (Sv1)

Turn off the power switch on the back of the main unit, then this valve opens to vent the exhaust line to the open air to prevent the pump oil from flowing back to the instrument when the rotary pump is in operation.

⚠ Be sure to turn off the power switch and vent the exhaust line to the open air, before you shutdown the pump. Otherwise, the pump oil may flow back to the main unit, which may cause failure.

⑦ Turbo molecular pump (TMP)

Attainable vacuum: 6.7 x 10^{-7} Pa or below (manufacturer's specification)

It makes a high vacuum in the system.

⚠ Do not shut down power to the main unit while the turbo molecule pump is in operation, or for 10 minutes after it stops. When power is removed during the operation, or immediately after the shutdown, the system pressure rises rapidly up to atmospheric pressure. It may apply overload to the turbo molecule pump, which may cause failure.

⚠ When accumulated operation time of the turbo molecule pump exceeds 20,000 hours, a maintenance work is prompted on the PC screen. Please contact our company if you find this message.
Accumulated operation time: 20,000 hours → Replace oil

ooo Measurement temperature device ooo

BELSORP-max has the measurement temperature devices as follow. Prepare the appropriate devices according to the desired pretreatment and measurement.

1. Dewar vessel

Dewar vessel

Volume: 2.6 L

Retention time: 60 hours

While sliding, install it to the **elevator hanger** ⑩ on the front of the main unit (P. 21).

⚠ The Dewar vessel is made of glass. Careful attention is required for the handling.
⚠ Do not drop the fitting into the Dewar vessel. It may cause a danger because the Dewar vessel glass is broken.
⚠ When removing the Dewar vessel with the sample cell still installed, be sure to move down the Dewar vessel to the bottom limit.
⚠ When installing to the main unit, slide it to the back limit until it is engaged with the fixing latch.
⚠ Do not use it as installed to different equipment (Our company shall not be liable for any accident or failure resulted from installing to different equipments.).

2. Water bath (optional)

1. General

The water bath temperature is maintained constant by circulating water or oil etc. using a circulating system (optional). While sliding, install it to the **elevator hanger** ⑩ on the front of the main unit (P. 21).

Two different types of water baths are available:

Open system: Temperature is controlled by circulating heat media between the circulating system and the water bath.

Closed system: The water bath has a dual-layered structure. The heat media temperature in the inner structure is controlled as to be constant by circulating heat media in the outer layer.

2. Specification

Temperature control method	Temperature is controlled using a temperature controller in the water bath.
Dimension and weight	W280 x H240 x D270 mm, 6 kg

3. Detailed description

① Detachable thermostatic bath set hole

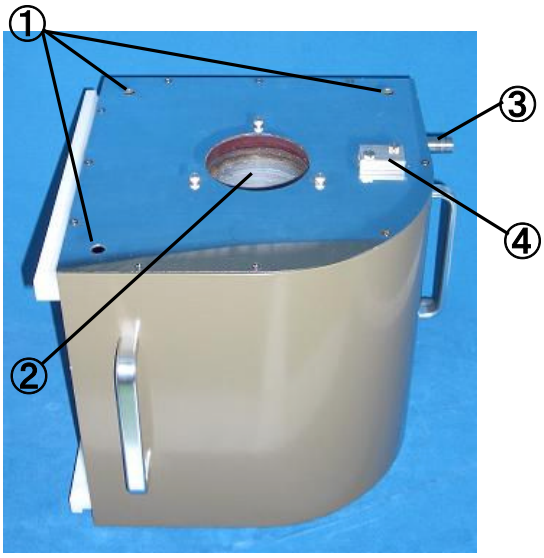
The accessory detachable thermostatic bath is set using these holes.

② Sample cell temperature control hole

When the water bath is lifted for installing to the BELSORP-max main unit, the sample cell enters to this hole.

③ Circulation hose connection port

Connect a hose from the circulation system (Port size: ϕ13 mm hose nipple).

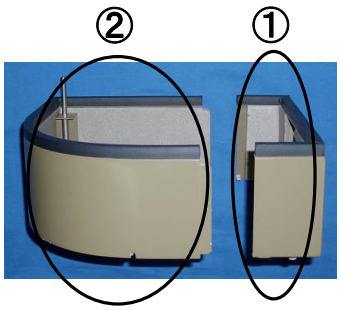


④ Thermometer fitting Attach a platinum temperature detector or a thermo couple to this fitting as required when measuring the water bath temperature or controlling temperature using an external sensor of the circulation system. Loosen the screws on the top of the electric furnace. Thermometer sandwichwed by the upper clamp, and tighten these two screws.	

4. Usage

1. Connect a hose from the circulation system to the circulation hose connection port ③ on the water bath.
2. Circulate the temperature-controlled heat media until the temperature is stabilized.
3. For the vapor adsorption measurement, install a liq. bottle to the adsorptive gas dosing port (Ads. 2) ⑨ on the front of the instrument (P. 21), and mount the accessory detachable thermostatic bath according to the following procedure.

How to mount the detachable thermostatic bath

 **Detachable thermostatic bath**		
Insert the part ① of the detachable thermostatic bath to the **detachable thermostatic bath set hole** ① on the top of the water bath.	Then, mount the part ② of the detachable thermostatic bath.	When it is complete, install the water bath to the instrument. When lifting the water bath, the detachable thermostatic bath opens the **needle valve adjustment screw storage shutter** ⑥ on the front of the main unit (P. 21), and the detachable thermostatic bath temperature is controlled.

⚠ When filling water to the bath, do not wet the instrument and the auxiliary equipments. Otherwise, it many cause rust on the instrument or short circuit of the internal electric equipment.
⚠ Connect firmly the hose from the circulation system.
⚠ When removing the Dewar vessel with the sample cell still installed, be sure to move down the Dewar vessel to the bottom limit.
⚠ When installing to the main unit, slide it to the back limit until it is engaged with the fixing latch.
⚠ When removing the detachable thermostatic bath with the sample cell still installed, be sure to prevent the sample cell from being broken.

3. Temperature controller

1. General

This is a control box to operate the 450 °C heater, 550 °C heater, and 1100 °C electric furnace for BELSORP-max. Connect a communication cable to the **Temp. cntl. computer port ⑧** on the back of the main unit (P. 22). Then the temperature setting can be adjusted from the controller and on the PC screen, and the pretreatment and measurement at high temperature can be controlled automatically.

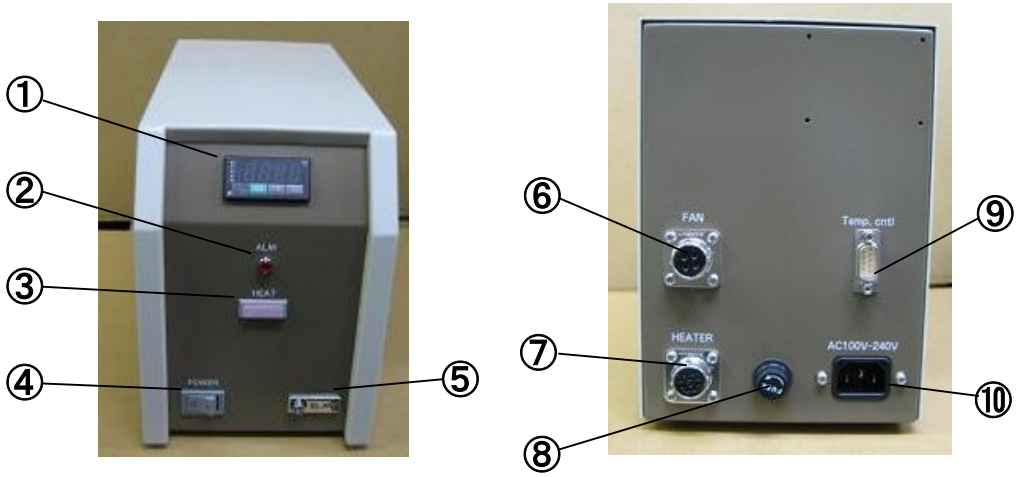
⚠ The heater and the peripheral equipment are hot while heating with the heater or immediately after the heating. Be careful to protect yourself from being burned.
⚠ The sample cell after heating is hot. Be careful to protect yourself from being burned.
⚠ Do not place any flammable material close to the heater while heating.
⚠ Be sure to install the "heat protection cover" on the heater, which is supplied with temperature controller, during heating and awhile after heating.
⚠ When heating up to high temperature using the 1100 °C electric furnace, be sure to use a quartz sample cell.

2. Specification

Temperature control method	PID control using a temperature controller
Dimension and weight	W145 × H200 × D300 mm, 4 kg
Power	AC100 V to 120 V or AC200 to 240 V, 600 VA (when using 550 °C heater)

⚠ Use single phase, AC power according to the specifications of the temperature measurement device.

3. Detailed description



① Temperature controller

This is used to display the current temperature and change the temperature setting. The temperature setting can be adjusted also from the PC screen.

In the case of overshoot is big, peform autotuning according to P. 34.

Default value of P : 5, Default value of I: 120, Default value of D : 20

② Overheat indicator

In case of overheat of the temperature controller, the overheat protection works to turn off heater automatically. In such a case, this LED lights up. The overheat protection works at the following temperature.

When using the 450 °C heater:	500 °C
When using the 550 °C heater:	600 °C
When using the 1100 °C electric furnace:	1150 °C

(When the overheat protection works, remove the cause and then supply power again to recover. In case the cause cannot be clarified, contact our company.)

③ Heater switch

This is a momentary type push button. Press this switch to start heating up to the temperature setting. This switch lights up while heating. Turning on/off heating can be controlled also from the PC screen.

④ Power switch

This is used to turn on/off the temperature controller.

⑤Power indicator

This indicates power supply to the temperature controller. It is interlocked with the power switch on the back of the temperature controller.

⑥ 4-pin female connector (for electric furnace rapid cooling fan)

Connect a 4-pin male connector from the 1100 °C electric furnace (It is not used except with the 1100 °C electric furnace.).

⑦ 10-pin female connector (for heater, electric furnace, thermocouple for temperature control, thermocouple for overheat prevention)

Connect the cable from the relevant temperature device.

⑧ Fuse

The fuse capacity is 10 A.

⚠ When a fuse blows out, remove the cause and replace the fuse. When recovering without removing the cause, it may result in short circuit.
⚠ Turn off the power switch before replacing a fuse.

⑨ Temp. cntl. connection port

D-sub 9-pin, male connector. Connect it to the optional temperature controller. Use a straight cable with D-sub 9-pin, male and D-sub 9-pin, female to connect to the main unit.

⑩ Power cable connection port

Connect a power cable of 110 V/220 V (Do not use wrong power supply.).

4. Usage

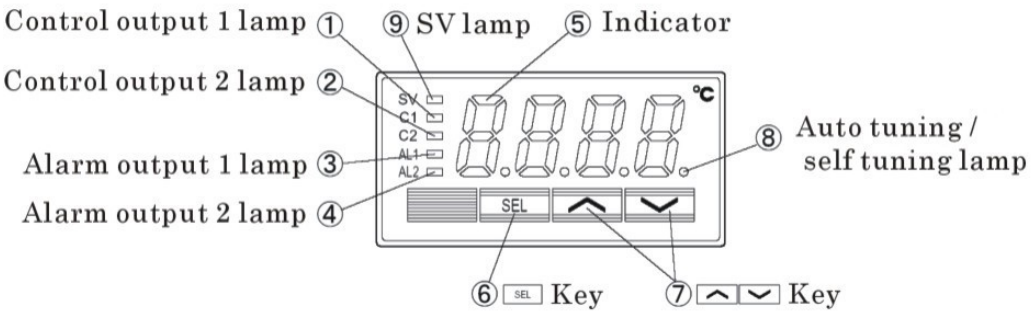
1. Verify that the **power switch ④** on the front of the temperature device controller is off, and connect power using the accessory power cable.

2. Connect a 10-pin male connector from the temperature device to the **10-pin, female connector ⑦** on the back of the temperature controller. When using the 1100 °C electric furnace, connect a 4-pin male connector to the **4-pin, female connector for the fan ⑥** on the back of a temperature controller.

3. Use the supplied straight cable with D-sub 9pin, male and D-sub 9-pin, female to connect to the **Temp. cntl. connection port** on the back of the temperature controller and the back of the main unit, respectively.

4. **Turn on the temperature controller after connecting as described above.** Then, the temperature setting can be performed on the PC. For the pretreatment, specify the parameters appropriately according to “ooo Pretreatment ooo, P. 122”. For the measurement, set the relevant parameters appropriately according to “ooo Setting the measurement parameter ooo, P. 128”.

Parts and function of Temperature controller



① **Control output 1 lamp**
It lights up when Control output 1 is ON.

② **Control output 2 lamp**
It lights up when Control output 1 is ON.

③ **Alarm output 1 lamp**
It lights up when Alarm output 1 is in operation. Also, it flashes on and off when ON delay is in operation.

④ **Alarm output 2 lamp**
It lights up when Alarm output 2 is in operation. Also, it flashes on and off when ON delay is in operation.

⑤ **Indicator**
PV (measured value) or SV (Set value) is displayed. However, parameter name or parameter value is displayed during parameter setting.

⑥ SEL **key**
It is used for switching between PV and SV, selection of parameter block, parameter selection and parameter confirmation.

⑦ **key**
It is used for changing SV, loading parameter and changing parameter.

⑧ **Auto tuning / self tuning lamp**
It flashes on and off during auto tuning or self tuning.

⑨ **SV lamp**
PV (measured value) is displayed normally (when it is not on). Pressing SEL key lights on SV and display SV (setting value). But it is off when displaying parameter or data.
It flashes on and off when the indicator displays PV(measured value) during standby.

1. How to set

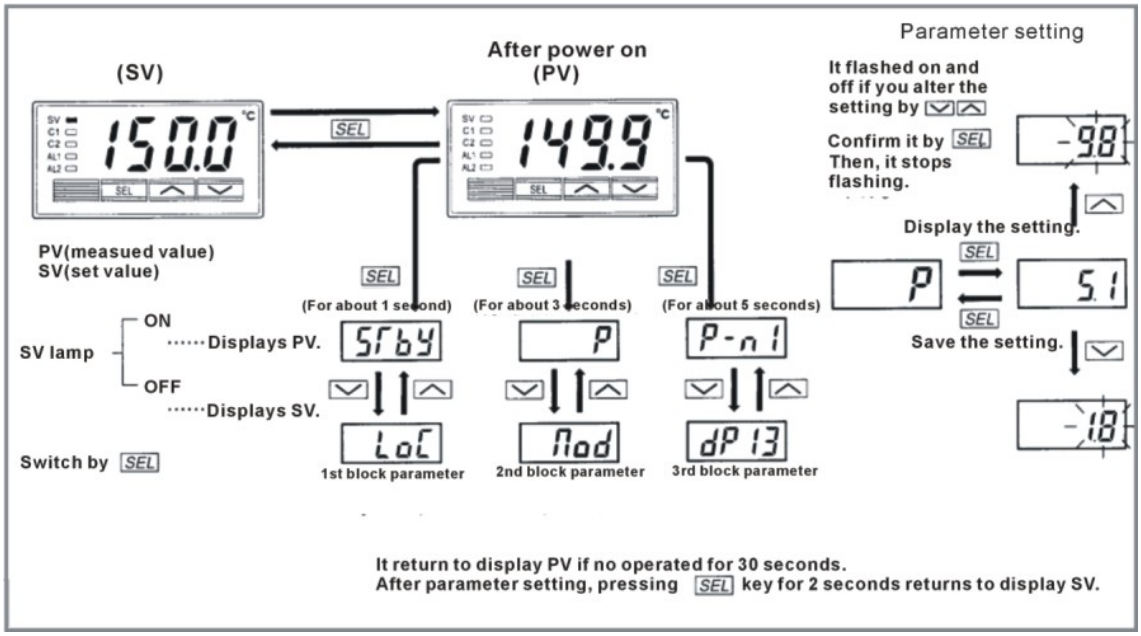
Change set point

- When current temperature is displayed, if SEL key is pressed SV lamp will lights up and set temperature will be displayed on the indicator. At this point, set temperature can be altered.
- Alter set point using ∧ and ∨.
- A new set point will be saved automatically approx. 3 seconds after changing, and the display will go back to indicate the current temperature.

⊘ Do not set the temperature over max. temperature of the each devices (450 °C heater : 450 °C, 500 °C heater : 500 °C, 1100 °C electric furnace : 1100 °C). It is very dangerous to unlock the protection and set a temperature over the max. temperature.

Parameter change

- Keep pressing SEL key for about 1 sec, 3 sec or 5 sec transfers to 1st, 2nd or 3rd block parameter relatively.
- Display desired parameter using ∧ and ∨.
- Pressing SEL displays set value.
- Alter set value using ∧ and ∨.
- Save a new set value by pressing SEL.



2. Parameters setting

Parameter display symbol	Parameter	Description	Setting range and default value	About set value
1st block parameter				
AT	Auto tuning	Used when P,I,D constant is set by auto tuning.	0: Stop 1: Standard AT Start 2: Low PV type AT start	Set to 1 or 2 when auto tuning is performed. It is automatically changed to 0 after auto tuning.
LoC	Key lock	Parameter setting: able to alter/ unable to alter	0,3: not locked (0: unlock) 1,4: not able to alter 2,5: able to alter only SV	Default value: 0
2nd block parameter				
P	Proportional zone	ON/OFF control Set to 0.0 for 2 position control	0.0 ~ 999.9%	Default value: 5
I	Integration time		0 ~ 3200 sec	Default value: 120
d	Differentiation time		0.0 ~ 999.9 sec	Default value: 20
3rd block parameter				
dSP1 ~ dSP9 dP10 ~ dP13	Parameter skip	Display/ not display setting	0 ~ 255	

3. Parameters

Auto tuning (setting range: 0/1/2)

- This is used for determining P, I, D parameters for temperature control automatically. Parameter is determined according to set point.
- If the power is switched OFF during auto tuning, auto tuning become of no use and P, I, D parameters does not change. If you want to restart set to 1 or 2 again.
- If you want to abort auto tuning, set to 0. Auto tuning will stop. P, I, D parameters does not change.
- Once P, I, D are set by auto tuning, it is no lot necessary to perform auto tuning ant more. The parameters are saved on the unit even if the power is OFF.
- If you set 1 or 2 auto tuning starts, and the value becomes 0 automatically after auto tuning is complete.
- The first decimal point of SV indicator flashes on and off during auto tuning.
- There are following types of auto tuning: Set code [1]: SV normal mode (ON/OFF control with SV as a standard), Set code [2]: Low PV mode (ON/OFF control with SV-10 %FS as a standard).
- [Note] since ON/OFF control is in operation during auto tuning overshoot against SV occurs. Please perform low PV mode auto tuning (Set code [2]) if you want to avoid overshoot.
- Auto tuning can be performed right after operation started, during control or during stable state.

4. Heater (450 °C Heater, 550 °C Heater)

1. General

This heater is installed to BELSORP-max, and used to control the sample section temperature. It enables the vacuum pretreatment and the adsorption measurement at high temperature.

2. Specification

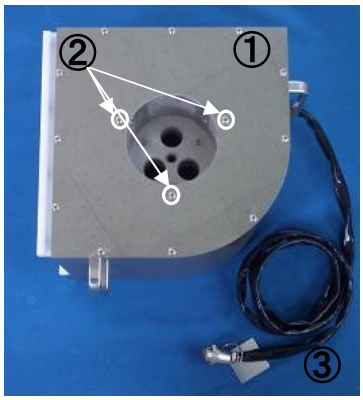
Specification	450 °C (Aluminum block)	550 °C (Brass block)
Number of ports	4 (including P0)	
Error between ports	±0.4 °C	±0.5 °C
Temperature range	50 to 450 °C	50 to 550 °C
Overheat detection temperature	500 °C	600 °C
Temperature stability	±0.2 °C	±0.5 °C
Dimension and weight	W280 x H300 x D270 mm, 6 kg	W280 x H300 x D270 mm, 9 kg
Power voltage	AC100 to120 V or AC200 to240V, 360 VA	AC100 to 120V or AC200 to 240 V, 600 VA

3. Detailed description

① Heater

4 holes for samples and saturation vapor pressure measurement are provided on the heater. When lifting up the heater for installing to BELSORP-max, the sample cell and the saturation vapor pressure cell are inserted in these holes. Align the sample cell with the hole by loosening the "heater alignment screw ②" before lifting up the heater.

⚠ Do not drop any material into the holes.



② Heater alignment screw

This is used to align the sample cell installed to the unit with the holes. Loosen the 3 screws to align in any direction with the holes. Alignment with the holes shall be made according to "Heater alignment" on the next page.

⚠ The sample cell or the saturation vapor pressure cell may be broken when lifting up the heater if misaligned with the heater holes. Be sure to align before use.

③ Heater control cable

Connect it to the temperature controller.

⚠ Prevent the cable from contacting heated parts while heating. If melted, it may cause short circuit.

4. Usage

1. Connect the **heater control cable** ③ to the **10-pin female connector** ⑤on the back of the temperature controller.

2. Slide and install it to the **elevator hanger** ⑩ on the front of the main unit.

⚠ When removing the heater with the sample cell still installed, be sure to move the heater down to the bottom limit.
⚠ When installing to the main unit, slide it to the back limit until it is engaged with the fixing latch.
⚠ Do not use it with other equipment.（Our company shall not be liable for any trouble.）
⚠ The heater and the peripheral equipment are hot while heating with the heater or immediately after the heating. Be careful to protect yourself from being burned.
⚠ The sample cell after heating is hot. Be careful to protect yourself from being burned.
⚠ Do not place any flammable material close to the heater while heating.
⚠ Be sure to install the “heat protection cover” on the heater, which is supplied with the temperature controller during heating and awhile after heating.

5. Heater alignment

Align the BELSORP-max sample cell with the heater holes as follows.

⚠ If misaligned, the sample cell may be broken when lifting up the heater. Be sure to align before use. Turn off the heater, and verify that it has been cooled down to room temperature before starting the alignment work.

1. Install a specially designed sample cell to BELSORP-max.
2. Loosen the **heater alignment screw** ②**.**
3. Lift up the heater step-by-step using the lifting button on the BELSORP-max main unit. Align the heater so that the sample cell and the P0 cell are inserted to the center of the holes. Once aligned, tighten the heater adjustment screw to fix the heater. (For use of the lifting button, refer to “Nomenclature and function of individual components, P. 21” in this manual.)
4. Lift down the heater, and tighten the **heater alignment screw** ② to fix the heater position.
5. Lift up the heater step-by-step, and verify again that the sample cell and the P0 cell are inserted to the holes. The alignment is now complete.

5. 1100°C electric furnace

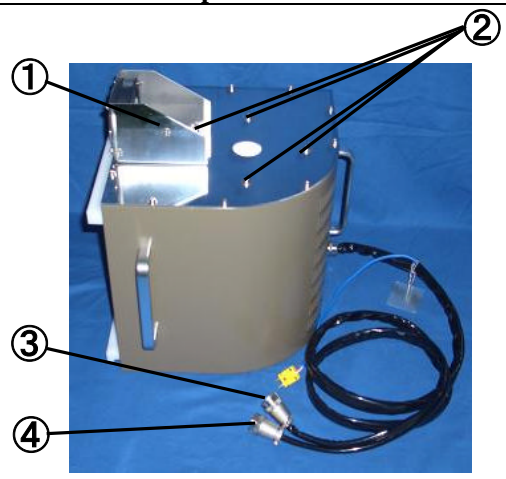
1. General

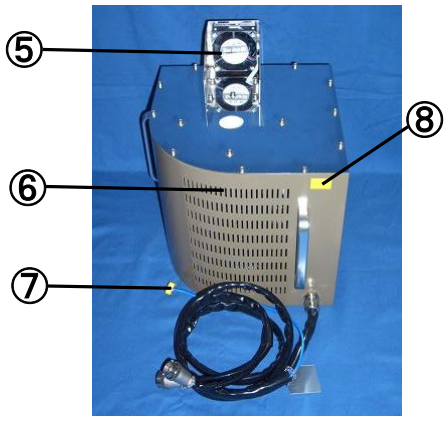
This heater is installed to BELSORP-max, and used to control the sample section temperature. This enables the vacuum pretreatment / flow gas pretreatment and the adsorption measurement at a high temperature up to 1100°C.

2. Specification

Number of ports	1
Temperature range	50 to 1100°C
Temperature stability	±0.5°C
Overheat detection temperature	1150°C
Dimension and weight	W280 x H300 x D270 mm, 6 kg
Power voltage	AC100V to 120V or AC200 to 240V, 330VA

3. Detailed description





① Electric furnace

The electric furnace has a hole to accommodate the sample cell. When lifting it up for installing to BELSORP-max, the sample cell installed to Port 3 is inserted to the hole. Align the sample cell with the hole by loosening the “heater alignment screw” before lifting it up.

⚠ When using the electric furnace, do not install the sample cell to Port 1 and 2 or a saturation vapor pressure cell.

② Electric furnace alignment screw

This is used to align the sample cell installed to the unit with the holes. Loosen the 4 screws to align in any direction with the holes.

⚠ The sample cell may be broken when lifting up the electric furnace if misaligned with the holes. Be sure to align before use.

③ Electric furnace control cable, ④ Rapid cooling fan control cable

Connect to the **10-pin, female connector** ⑦ and **4-pin, female connector** ⑥ (for rapid cooling fan) on the back of the temperature controller, respectively (P. 31).

⚠ Prevent the cable from contacting hot parts while heating. If melted, it may cause short circuit.

⑤ Upper fan

This fan is installed to the electric furnace for releasing heat from the heating port while heating. Connect the **electric furnace control cable** ③, and turn on the temperature controller. This starts automatic operation.

⑥ Rapid cooling fan

A fan is equipped inside. Connect the **electric furnace control cable** ③ and the **rapid cooling fan control cable** ④. When the electric furnace temperature exceeds 1150 °C, the system turns off the electric furnace and starts the rapid cooling fan. When setting FAN as ON on the software "Vacuum/flow gas sequential pretreatment" screen, this rapid cooling fan starts (For the above mentioned pretreatment, refer to P. 122).

⑦ Control thermometer connector (male)

For internal temperature control (temperature control using a thermometer in the electric furnace), connect this to the **internal temperature control thermometer connector (female)** ⑧ on the electric furnace. For external temperature control (temperature control using a thermometer that is inserted to the accessory flow gas sample cell thermometer sheath), connect this to the accessory external temperature control thermometer connector (female).

It is recommended to use the external temperature control for more accurate temperature control of the sample section. When using the internal temperature control, calibrate the internal temperature by measuring the sample section temperature using another thermometer.

⑧ Internal temperature control thermometer connector (female)

Connect the **control thermometer connector (male)** ⑦ when using the internal temperature control. Do not connect anything to this connector when using the external temperature control.

4. Usage

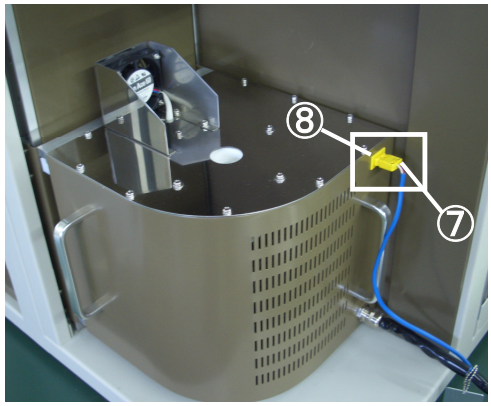
1. Connect the electric furnace control cable ③ and the rapid cooling fan control cable ④ to the 10-pin, female connector ⑦ and 4-pin female connector ⑥ on the back of the temperature controller (P. 31), respectively.
2. While sliding, install it to the **elevator hanger** ⑩ on the front of the main unit (P. 21).

⚠ When removing the electric furnace with the sample cell still installed, be sure to move the electric furnace down to the bottom limit.
⚠ When installing to the main unit, slide it to the back limit until it is engaged with the fixing latch.
⚠ Do not use it with other equipment (Our company shall not be liable for any trouble.).
⚠ The electric furnace and the peripheral equipment are hot while heating with the electric furnace or immediately after the heating. Be careful to protect yourself from being burned.
⚠ The sample cell after heating is hot. Be careful to protect yourself from being burned.
⚠ Do not place any flammable material close to the electric while heating.
⚠ Be sure to install the "heat protection cover" on the electric furnace while heating, which is supplied with the temperature controller.
⚠ Be sure to use quartz sample cell when heating up to high temperature with the electric furnace.

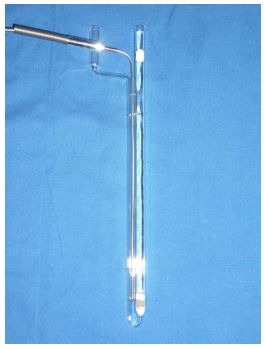
3. According to the control method used, connect the relevant connector as follows.

For internal temperature control

Connect the **control thermometer connector (male)** ⑦ to the **internal temperature control thermometer connector (female)** ⑧ as shown on the right.



For external temperature control

		
Connect the external temperature control thermometer connector (female), an accessory of the 1100 °C electric furnace, to the **control thermometer connector (male)** ⑦.	Insert the thermometer to the flow gas sample cell thermometer sheath (Bend the thermometer at an angle of 90 degrees as appropriate.).	Install the flow gas sample cell to the main unit. For installation, refer to "How to install the flow gas sample cell (optional), P.59".

5. Electric furnace alignment

Align the BELSORP-max sample cell or the flow gas sample cell with the electric furnace as follows.

⚠ If misaligned, the sample cell may be broken when lifting up the heater. Be sure to align before use. Turn off the heater power, and verify that it has been cooled down to room temperature before starting the alignment work.

1. Install the sample cell or a flow gas sample cell to the BELSORP-max, Port 3.
2. Loosen the electric furnace alignment screw on the top of the electric furnace.
3. Lift up the electric furnace step-by-step using the lifting button on the BELSORP-max main unit. Align the electric furnace so that the sample cell is inserted to the center of the holes. Once aligned, tighten the electric

furnace adjustment screw to fix the electric furnace (For use of the lifting button, refer to “Nomenclature and function of individual components, P.21” in this manual.).

4. Lift down the electric furnace, and tighten the electric furnace alignment screw to fix the electric furnace position.
5. Lift up the electric furnace step-by-step, and verify again that the sample cell or the flow gas sample cell is inserted to the holes. The alignment is now complete.

ooo Manual-switching gas selector (Option) ooo

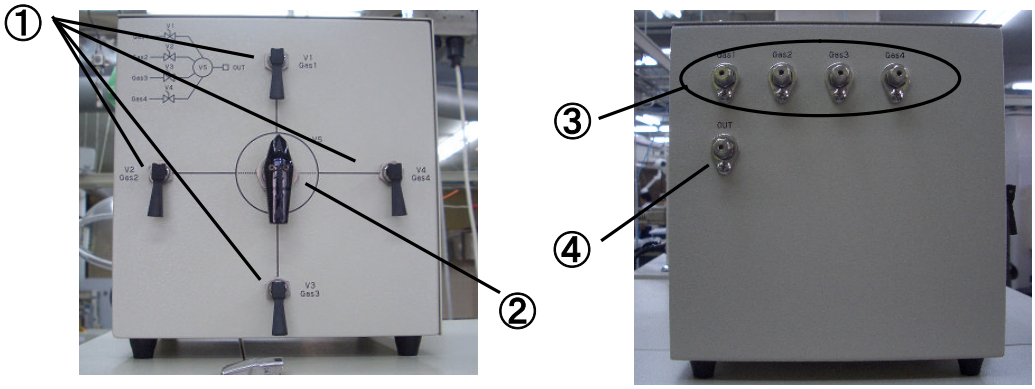
1. General

This instrument is an accessory to switch the gas introduced into BELSORP-max by manual operations of the valves.

2. Specification

Available gas	N_2, Ar, Kr, H_2, CO, O_2, CH_4, other non-corrosive gas
Material of joint	SUS, brass
Gas port	4 at inlet, 1 at outlet (joint: 1/8” SWG)
Pressure	0.1 MPa (G)
Dimension	W240×H240×D240 mm (except the projection of the valve)

3. Detailed description



①Switching valves (V1 to V4)

Gas supply to the tubes connected with Gas 1 to Gas 4 is started/stopped by these manual-switching valves.

②Gas switching valve (V5)

Gas supplied to BELSORP-max is selected by this rotary-type manual-switching valve.

③Gas inlets (Gas 1 to Gas 4)

Gas is supplied from here to the main unit.

④Gas outlet (OUT)

The gas supplied to the main unit is exhaust from this outlet.

4. Usage

1. How to connect the tube

①Close the switching valves on the front panel (V1 to V4). The valves are closed by bringing down the cocks.

②Connect the gas outlet (OUT) on the side panel with Aux. 1 to Aux. 4 and Ads. of BELSORP-max.

③Connect the gas to be used with the gas inlets (Gas 1 to Gas 4) on the side panel.

⚠ Adjust the secondary pressure of the gas cylinder to 0.1±0.01 MPa (1kg cm^{-2}).

2. Washing the gas line

①Open a switching valve (one of V1 to V4), and turn the gas switching valve (V5) to the line to be washed.

②Select a line, and wash the gas line as referring to “Installing and replacing gas cylinders, P. 83”.

3. How to switch gas

①Close the switching valve which has been used (one of V1 to V4).

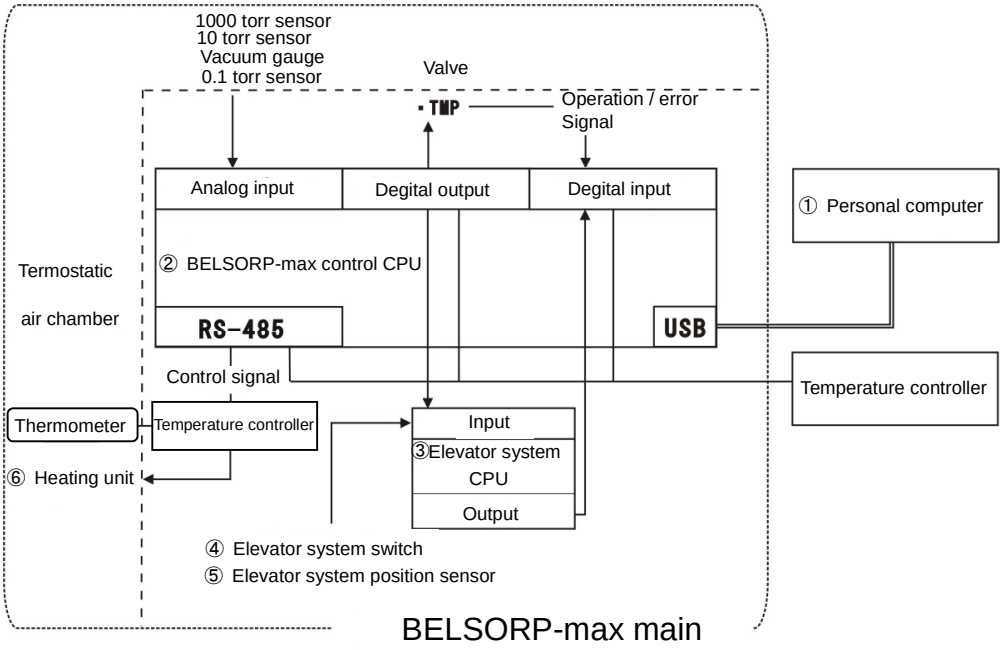
②As referring to “Installing and replacing gas cylinders, P. 83”, wash the gas line up to the switching valve (one of V1 to V4).

③Turn the gas switching valve (V5) to the line to be used.

④Open the switching valve of that line (one of V1 to V4), and wash the gas line as referring to “Installing and replacing gas cylinders, P. 83”.

⚠ To avoid gas from blending, be sure to wash the gas line before switching gas.

ooo System configuration ooo



① Personal computer

It use specialized measurement software for thefolowing controls. It communicates with the main unit via USB.

· Operating and closeing valve
· Reading pressure in the system
· Operating the vacuume gauge
· Operating the turbo molecular pomp
· Operating the elevator
· Reading temperature of the thermostatic air snd temperature device
· Operating the temperature controller

② BELSORP-max control CPU

This is a computer built in main unit. It recives signals from the personal computer to control various functions.

③ Elevetor system CPU

This is a computer bilut in main unit. It recives from the lifting switch on the front of main unit and the personal computer to control the elevator.

④ Elevator system switch

It consists of the [▲] (lift-up) switch and [▼] (lift-down) switch. For details, refer to “ooo Main unit-front ooo, P. 21”.

⑤ Elevator system position sensor

This detects that the elevator has moved down to the bottom limit.

⑥ Heating unit

This unit located in the thermostatic manifold temperature. It integrates a fan and heater, and controls automatically the thermostatic aie chamber temperature to be 40 ^{o}C (Option 50 ^{o}C), when the main unit switch is turned on.

Caution

Do not use a pump with a maximum operating current of more than 7A.

Do not turn off power to the pump with the main unit switch turned on. Otherwise, oil may flow back to the instrument, which may contaminate inside the unit.

The Dewar vessel or the temperature unit moves up and down during the sample measurement. Do not place your fingers or any materials on the Dewar vessel or the temperature unit. It may cause bodily injury and/or instrument failure.

Do not press the lifting switch during the sample measurement using refrigerant. When lifting the Dewar vessel out of necessity during the sample measurement, careful attention is required as follows.

When lifting down the Dewar vessel, it returns from the refrigerant temperature to room temperature. At this moment, the nitrogen or argon that is adsorbed or condensed to the sample section or at the saturation vapor pressure P0 port may evaporate, and generate higher pressure than atmospheric pressure. This may cause an error of the measurement data, but also result in damage to the instrument since it raises pressure in the glass tube, and detaches it from the instrument connection port over time. This measurement software stops forcedly the sample measurement and degasses the system automatically, when the measurement port pressure exceeds 130 kPa.

Prior to measurement, install the heat insulation cap after removing the ice or water adhering to it.

BELSORP-max installation

ooo BELSORP-max package items and other requisites ooo

1. BELSORP-max package items

Standard BELSORP-max includes the main unit and accessories as follows. Please verify that the complete accessories are provided. If you find any items missing or damaged, please contact our company.

Main unit or accessories		Quantity
-	BELSORP-max main unit	1
①	Ads. 2 conversion connector (Connect to the "adsorptive gas dosing port (Ads. 2) " on the front of the unit).	1
②	Power cable	1
③	Communication cable (USB cable)	1
④	Rotary pump*	1
⑤	NW16 flexible tube*	1
⑥	NW16 clamp*	2
⑦	NW16 centering*	2
⑧	Dewar vessel	1
⑨	Dewar vessel heat insulation lid	1
⑩	Sample cell heat insulation sleeve (to be used when using the Dewar vessel)	6
⑪	P0 cell heat insulation sleeve (to be used when using the Dewar vessel)	1
⑫	P0 cell o-ring Securing screw	1 2 1
⑬	P0 port cap	1
⑭	Sample cell weighing stand (to be used as the sample cell holder on a balance pan when measuring the sample weight)	
⑮	Sample cell stand	1
⑯	Reference sample (0.2 g) (non-porous carbon black A_{BET} = 49.17 ± 1.5 $m^2 g^{-1}$, P/ P_0 : 0.04-0.15)	1

*: Different depending on the pump specification


①Ads.2 conversion connector


②Power cable


③Communication cable


④Rotary pump

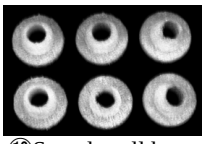

⑤NW16 flexible tube


⑥NW16 clamp


⑦NW16 centering

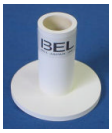

⑧Dewar vessel


⑨Dewar vessel heat insulation lid


⑩Sample cell heat insulation sleeve


⑬P0 port cap


⑫P0 cell (right)
o-ring (upper left)
Securing screw (lower left)

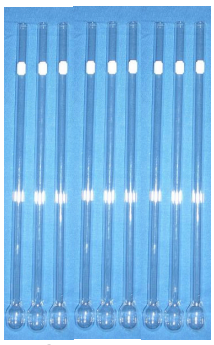

⑭Sample cell weighting stand


⑮Sample cell stand

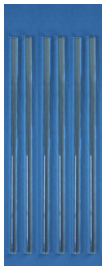

⑯Sample cell weighting stand

	Accessories	Quantity
⑰	Port plug	4
⑱	Sample cell (Pyrex) (Op. silica)	9
⑲	Glass rod (Pyrex) (Op. silica)	6
⑳	Sampling funnel	3
㉑	Liq. bottle (Pyrex)	1
㉒	Dewar vessel	1
㉓	FKM O-ring (Op. FFKM)	6
㉔	Sample scattering prevention filter	6
㉕	Sample cell cap	10
㉖	Instruction manual (this manual)	1
㉗	Analysis software manual	1
㉘	Instruction manual-Supplement (Measurement example)	1
㉙	Setup CD	1
㉚	Config CD (Instrument specific data is stored, including the reference volume. Keep this carefully.)	1
㉛	WIBU-key (for analysis software to recognize effective software)	1

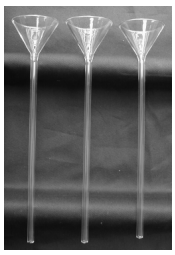
⑰Port plug



⑱Sample cell



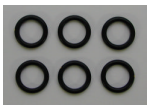
⑲Glass rod



⑳Sampling funnel

㉑Liq. bottle

㉒Dewar vessel



㉓P9 o-ring

㉔Sample scattering prevention filter (P-9)

㉕Sample cell cap (ϕ9)

㉖Instruction manual

㉗Analysis software manual

㉘Instruction manual-Supplement

㉙Setup CD

㉚Config CD

㉛WIBU-key

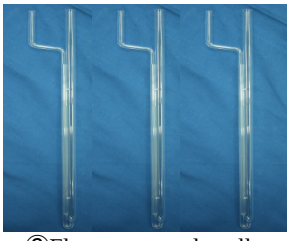
2. Optional equipment

The following options are available separately from the standard package.

Accessories	
①	Sample cell (silica)
②	Glass rod (silica)
③	Flow gas sample cell (Pyrex or silica)
④	Silica glass wool
⑤	Small volume sample cell*1
⑥	Glass rod for small volume sample cell*2
⑦	Large volume sample cell*1
⑧	Glass rod for large volume sample cell*2
⑨	Pellet sample cell*1
⑩	Glass rod for pellet sample cell*2
⑪	Quick seal*1
⑫	Glass rod for quick seal*2
⑬	NSD capusle*2
⑭	NSD capusel sample cell

*1 Standard glass rods cannot be used.

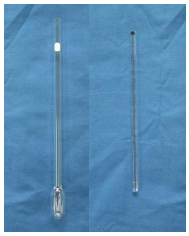
*2 Standard sample cell cannot be used.



③Flow gas sample cell

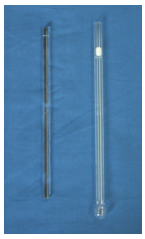
④Silica glass wool

⑤Small volume sample cell
⑥Glass rod for small volume sample cell



⑦Large volume sample cell
⑧Glass rod for large volume sample cell

⑨Pellet sample cell
⑩Glass rod for pellet sample cell



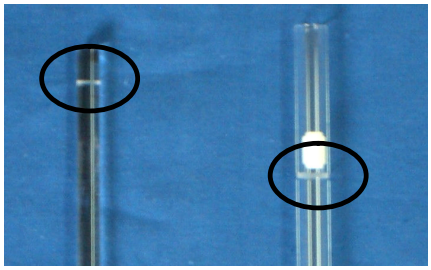
①Sample cell (silica)
②Glass rod (silica)

⑫Glass rod for quick seal

⑪Quick seal

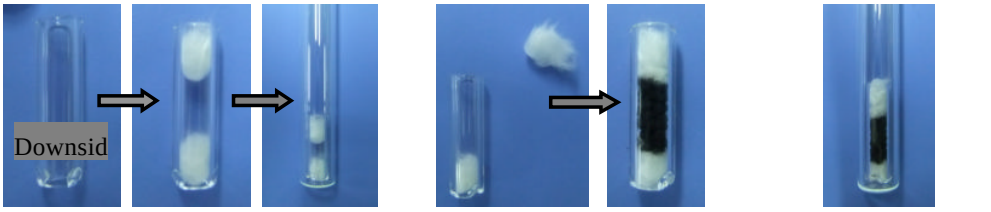
⑬NSD capusel
⑭NSD capusel sample cell

Silica glass devices are marked with a white line as shown below for identification.



■Usage of NSD capsule

1. Blank weight measurement → 2. Sample packing → 3. Pretreatment start



NSD capsule

A dedicated sample cell and a glass rod (Pay attention to direction.)

Take upper glass wool out.

Sample packing

Set it in the sample cell.

Measure the blank weight with silica wool inside. To pack the sample, stand the NSD capsule with a dent side down, place the sample on the silica wool in the NSD capsule as shown above, and insert upper silica wool that was taken out. Place the NSD capsule in which the sample is packed in the sample cell for NSD capsule, put a glass rod.

Water bath

Accessories	Quantity
Water bath	1
Detachable thermostatic bath	1

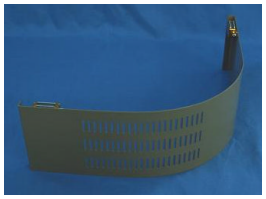
Temperature controller

Accessories	Quantity
Temperature controller	1
Power cable	1
Communication cable (D-sub 9 pin straight cable)	1
Heater protection cover (to be installed on the top of the heater when using the heater)	1

.

Temperature controller

Power cable

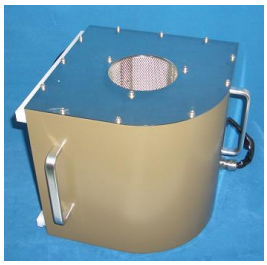


Heater protection cover

Communication cable

450 °C heater

Accessories	Quantity
450 °C heater	1



450 °C heater, 550 °C heater

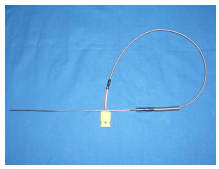
550 °C heater

Accessories	Quantity
550 °C heater	1

1100 °C electric furnace

Accessories	Quantity
1100 °C electric furnace	1
External temperature control thermometer	1

1100 °C electric furnace



External temperature control thermometer

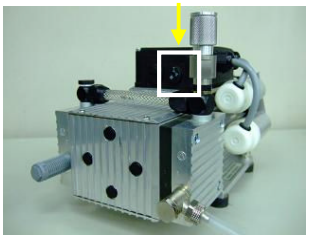
Diaphragm pump

Accessories	Quantity
Diaphragm pump	1

Diaphragm pump

The diaphragm pump is equipped with a voltage switch.

Switch voltage in accordance with the place of use before using the pump.



Corrosion resistant diaphragm pump

Accessories	Quantity
Corrosion resistant diaphragm pump	1
Flexible tube	1
Flexible tube connection clamp	2
Flexible tube connection centering	2

Corrosion resistant diaphragm pump

Flexible tube

Clamp

Centering

Corrosion resistant rotary pump

Accessories	Quantity
Corrosion resistant rotary pump	1
Flexible tube	1
Flexible tube connection clamp	2
Flexible tube connection centering	2

Corrosion resistant rotary pump

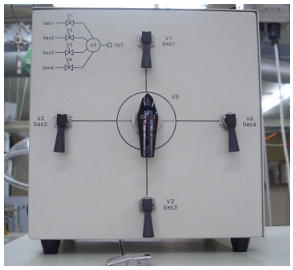
Flexible tube

Clamp

Centering

Corrosion resistant gas selector

Accesories	Quantity
Gas selector unit	1
Earthquake resistant stopper	1
Magnetic sheet	4



Corrosion resistant gas selector

3. Utility and other requisites

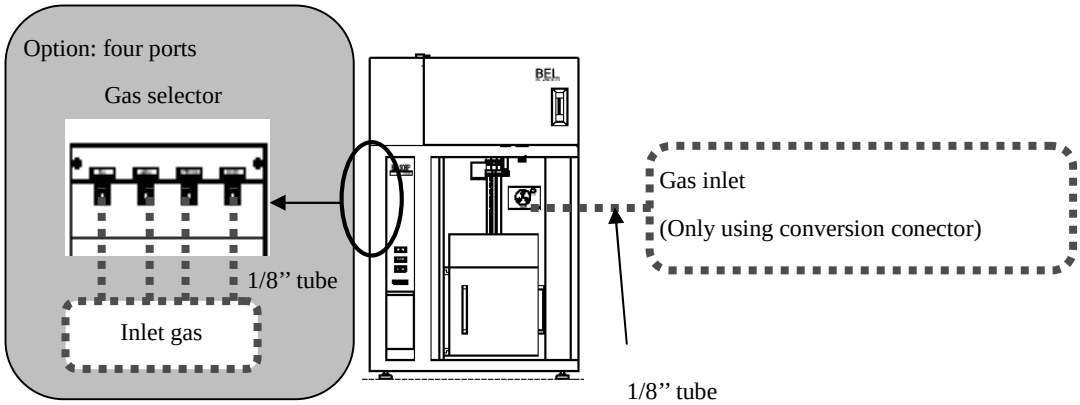
BELSORP-max requires the following utilities. Provide them appropriately according to the following "Requirements". Personal computers are also available from our company.

Requisites		Requirements
Personal computer		Refer to "System environment required, P. 75".
Dosing gas	To be provided by the customer	Purity : Use the products of purity 99.999 % or more Pressure : 0.1 MPa (gauge pressure) Connection : 1/8'' Swage lock
Helium gas		Purity : Use the products of 99.999 % or more Pressure : 0.1 MPa (gauge pressure) Connection : 1/8'' Swage lock
Air and gas to drive pneumatic valves		Pressure : 0.5 to 0.6 MPa (gauge pressure) Connection : 1/4'' plastics tube quick connect
Vent line		Connection : 1/8'' Swage lock

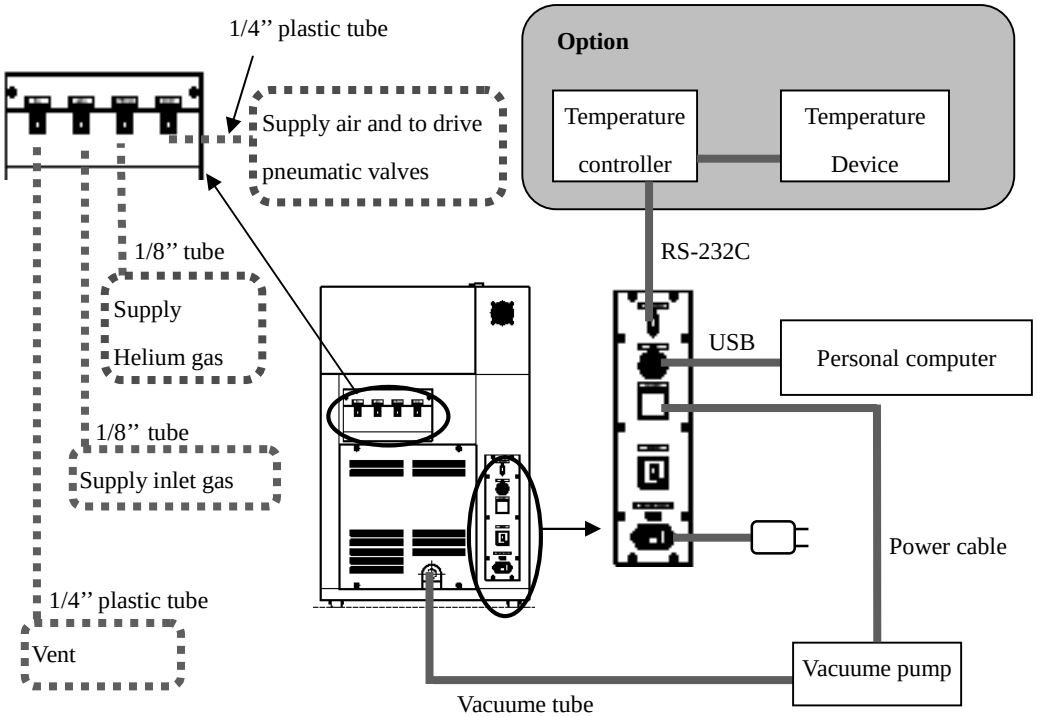
: Part packaged as an accessory of BELSORP-max or its options

: Part needing to be prepared separately

(Such parts are not included in the accessories of BELSORP-max and its options. You need to prepare them or request us to prepare them.)



Main unit-front



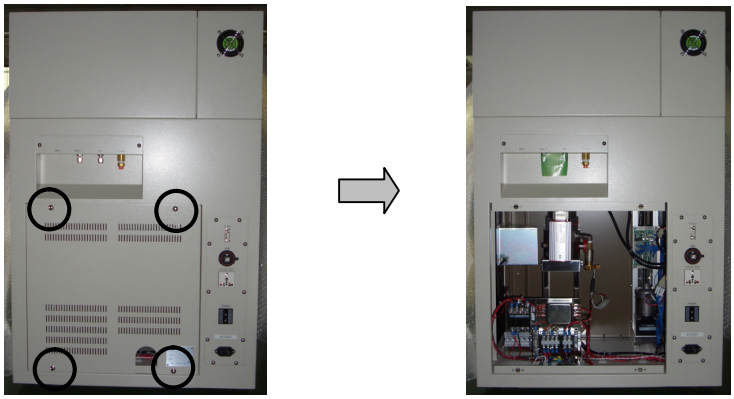
Main unit-back

ooo Installation procedure ooo

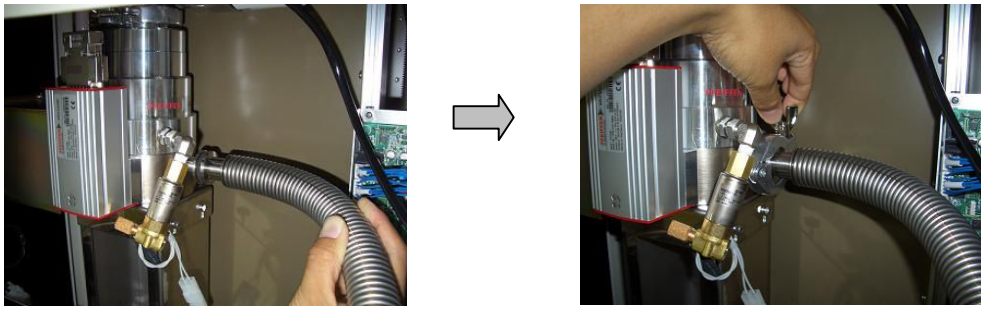
1. Connection with auxiliary equipment

1. Place the **BELSORP-max** main unit on a horizontal place, and verify that it seats stably.

2. Remove the access door on the back of the instrument. Turn the slot on the latch lock (at 4 locations) to the vertical direction using a flat head driver. The lock is then released. Pull out the door to remove.



3. Attach the flexible tube to the turbo molecular pump located deep on the back of the unit. Insert the accessory "flexible tube connection centering (NW16)" between the "flexible tube" and the turbo molecular pump connection port, and fix it using the "flexible tube connection clamp (NW16)". Lastly, firmly tighten the screw on the clamp.



4. Replace the access door in place, which was removed in **2.** In this step, lead the "flexible tube" out of the instrument through the hole on the access door.

5. Connect the other end of flexible tube to the rotary pump suction port.

⚠ Oil mist is discharged from the pump exhaust port. Process it appropriately.

⃠ Do not connect any pump with voltage except those specified on the nameplate on the back of the instrument.

6. Connect the rotary pump power plug to the AC outlet on the back of the main unit.

7. Install an exhaust line to the vent port.

The main unit connection port uses a 1/4” plastics tube quick connect only when the optional flow gas pretreatment line is selected.

> ❗ It is dangerous to perform flow gas pretreatment without an exhaust line attached to the vent port, since used gas is discharged. When performing the flow gas pretreatment, be sure to attach an exhaust line to the vent port.

8. Connect a gas line of the adsorptive gas (0.1 Mpa (gauge pressure)). The main unit connection port uses a 1/8’’ Swage lock.

9. Connect a gas line of helium gas (0.1 MPa (gauge pressure)). The main unit connection port uses a 1/8’’ Swage lock.

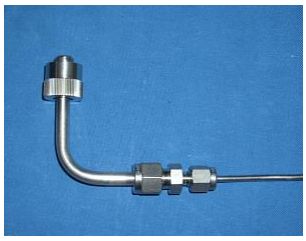
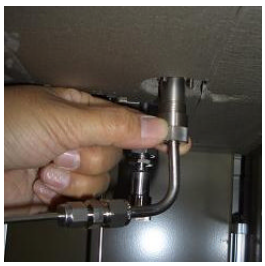
10. Supply air and gas (to drive pneumatic valves, 0.5 to 0.6 MPa). The main unit connection port uses a 1/4” plastics tube quickly connect.

11. Use a USB cable to connect the USB connector on the personal computer to the USB connector (type-B, female) on the main unit.

12. Connect the power source specified on the nameplate on the back of the main unit.

2. How to connect the gas line to the “adsorptive gas dosing port (Ads.2)”

1. When supplying gas from the Ads.2 port on the front of the main unit, connect the relevant gas line as follows.

		
Connect the gas line of adsorptive gas (0.1 MPa gauge pressure) to the “Ads. 2 conversio connector” provided.	Attach an o-ring to the “Ads. 2 conversion connector”, and insert it to the “adsorptive gas dosing port (ads. 2)” until it contacts a metal part on the back.	Tighten a nut on the “Ads. 2 conversion connector” by hand. Connection is now complete.

3. How to connect the gas line to the “gas selector (optional)”

Connect a gas line of the dosing gas (0.1 MPa (gauge pressure)). All ports use the 1/8’’ Swage lock.

4. How to install the sample cells and liq. bottles

- Use the same type of sample cells, dead volume reference cells, and glass rods.
- For sample measurement, insert a glass rod both to the sample cell and the dead volume reference cell. Slide down the glass rod slowly along the glass wall so that the glass tube is not broken.
- Before using sample cells, glass rods, and a liq. bottle ; wash and dry them sufficiently.
- Store them in a desiccator after washing.

⚠ The sample cells and the liq. bottles are made of glass. Careful attention is required for the handling.

Sample cell

Glass rod

P0 cell (right)
o-ring (upper left)
Securing screw
(lower left)

1. Insert a glass rod to both the sample cell and the dead volume reference cell (when measuring the dead volume).

2. Install the sample cell after removing a fitting and o-ring from it. When the sample cell is installed with the fitting still attached, it may deform the o-ring, and accordingly it may result in vacuum leakage. When removing the sample cell from the instrument, Viton o-ring may remain inside the connection port of the instrument. Verity that there is Viton o-ring remaining inside the connection port.

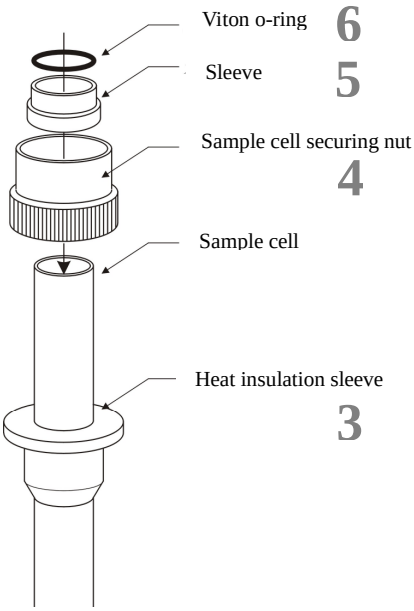
⚠ Do not drop any fitting into the Dewar vessel. It may be dangerous because the Dewar vessel glass will break.

3. Attach the heat insulation sleeve to the sample cell as shown on the right.

4. Attach the sample cell securing-nut. Do not use upside down.

⚠ Do not use a heat insulation sleeve when using a heater for pretreatment or measurement. Otherwise, it may cause a fire.

5. Attach the sleeve. Do not use upside down.

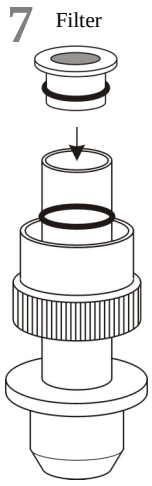


6. Attach Viton o-ring. The measurement section is sealed with this o-ring pressed on the sample cell and the measurement ports. When the o-ring is damaged, or any foreign material is pressed with the o-ring, air may flow in the measurement section. This may affect data accuracy. Be sure that no foreign material is contained. Replace the damaged o-ring, if any, with a new one.

7. Insert the filter from the top of the sample cell.

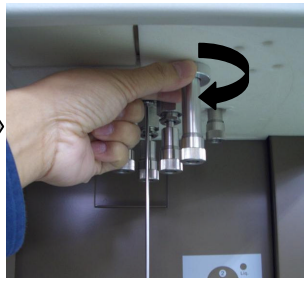
8. Hold the sample cell firmly, and insert it to the sample port until it contacts the metal wall in the fitting. Tighten the sample cell securing-nut by hand.

9. Slide the heat insulation tube halfway down the sample cell. The liq. bottle is installed in the same way as the sample cell, but no heat insulation sleeve (3.), filter (7.) are required in this case.



5. How to install the flow gas sample cell (optional)

1. There are 2 connection ports for installing the flow gas sample cell. Prior to installing the sample cell, align the connection port with the sample cell as follows.

		
Loosen a nut on the flow gas pretreatment line (optional) on the front of the main unit, so that the flow gas pretreatment line can be moved.	Place a flow gas sample cell from the bottom, and align the flow gas pretreatment line with it.	After aligning the flow gas pretreatment line, tighten the nut to fix the flow gas pretreatment line position. Alignment is now complete.

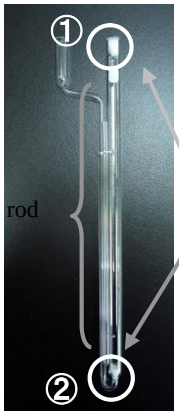
⚠ The flow gas sample cell is made of glass. Careful attention is required for the handling.

2. Attach the sample cell securing-nut, sleeve, and o-ring to the flow gas sample cell according to " How to install the sample cells and liq. bottles on P. 57".

6. Sampling procedure when using a flow gas sample cell

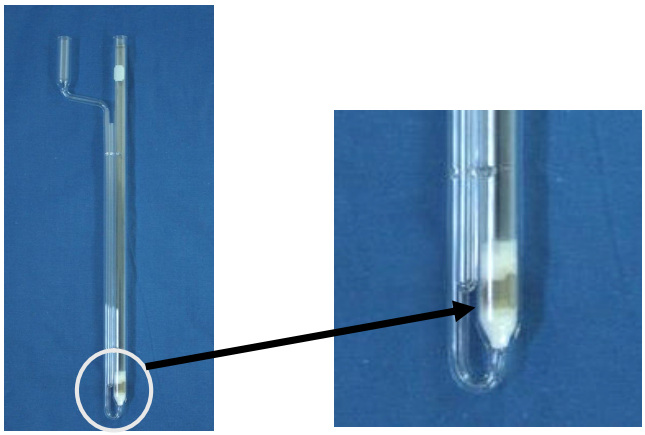
When using a flow gas sample cell, use the silica glass wool, an accessory of the flow gas pretreatment line (optional) to perform the following sampling procedure.

1. Prepare two appropriate sized balls of silica glass wool (standard: 0.01 to 0.02 g).
2. Insert them and a glass rod in the flow gas sample cell as shown in the photo on the right (Measure the blank weight at this time).



3. Remove the silica glass wool ① and a glass rod, and feed a sample on the silica glass wool ② using a funnel.

4. Replace the silica glass wool and a glass rod ① (Measure the sample weight at this time).

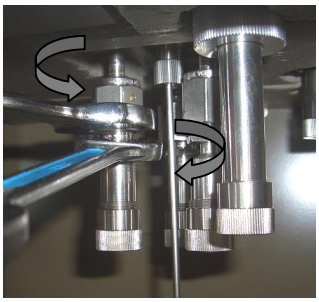
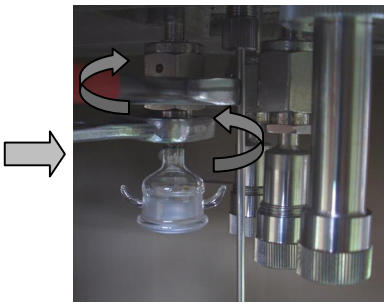
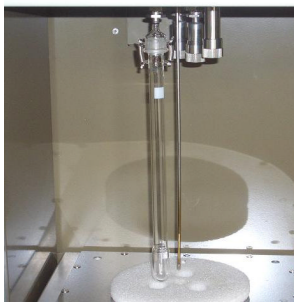


⚠ When using silica glass wool, careful attention is required for the handling as follows.

- When handling the glass wool, take appropriate measures for local exhausting because dust is easily scattered.
- Use a dust mask.
- Do not handle it with bare hands.
- When the wool adheres to your clothing, remove it completely.
- After handling, gargle and wash your hands sufficiently.

7. How to install the pellet sample cell (optional)

Install the pellet sample cell as follows.

		
Remove the port to be installed using two wrenchs, and remove the 4VCR gasket.	Place the 4VCR gasket on the 4VCR at the upper part of the pellet sample cell, and install it to the instrument.	Insert the glass rod for the pellet sample cell into the sample section of the pellet sample cell, install it to the instrument, and secure it with a spring. Installation is now complete.

8. How to install/remove the Dewar vessel, temperature measurement device

⚠ The Dewar vessel is made of glass. Careful attention is required for the handling.

⚠ When removing the Dewar vessel temperature device with the sample cell still installed, be sure to move down the Dewar vessel temperature device to the bottom limit.

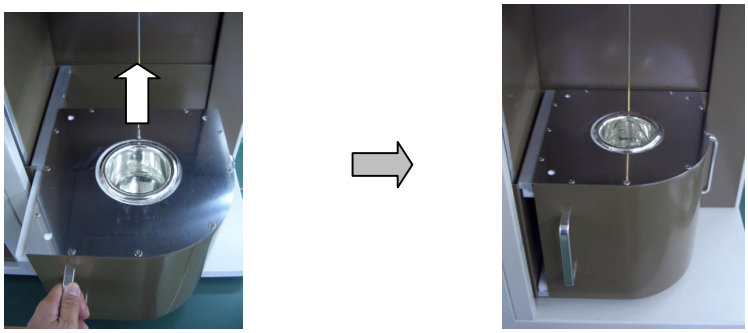
⚠ When installing to the main unit, slide it to the back limit until it is engaged with the fixing latch.

⚠ The heater and the peripheral equipment are hot while heating with the heater or immediately after the heating. Be careful to protect yourself from being burned.

⚠ The sample cell after heating is hot. Be careful to protect yourself from being burned.

⚠ Be sure to install the "heat protection cover" on the heater or the electric furnace while heating, which is supplied with the temperature controller.

1. Insert the slide rail on the side of the Dewar vessel temperature device to the "elevator hanger" on the front of the main unit, and slide it to the back.



2. Slide it to the back limit, until it is engaged with the fixing latch.
3. When removing the Dewar vessel temperature device from the main unit, move the Dewar vessel temperature device down to the bottom limit, and pull the handle.

9. Conversion of the flow meter value by gas type

The flow meter value indicated at the upper right of the instrument front panel varies depending on the gas type; therefore, convert it appropriately using the following equation.

(Example) When applying a H_2 (hydrogen) flow meter to He (helium), the actual flow rate should be smaller than the indication, as follows.

$$QHe = QH_2\sqrt{\frac{\rho H_2}{\rho He}} = QH_2\sqrt{\frac{2}{4}} \fallingdotseq 0.7QH_2$$

Q: Flow rate [$cm^3\ sec^{-1}$]

ρ: Density of liquid [$g\ cm^{-3}$]

10. Safety devices

BELSORP-max is equipped with the following safety devices. When any safety device is activated, it takes actions automatically as follows. Reset it as listed below after you remove the cause.

Safety device	Action	How to reset
Manifold temperature overheat detection	When the temperature in the manifold temperature on the top of the instrument exceeds 90 °C, it detects faults and turns off the instrument power.	When the temperature in the manifold temperature drops below 90°C, turn off the power switch on the back of the instrument, and then turn it on again to reset.
Temperature device overheat detection	When the temperature device (450 °C heater, 550 °C heater, 1100 °C electric furnace) exceeds the specified temperature (for details refer to the temperature controller on P. 32), the temperature controller detects faults and stops heating (in such a case, the "overheat indicator" on the front of the temperature controller lights up). When the measurement software is running, it exits automatically.	After cooling the temperature device, turn off the power switch on the front of the temperature controller, and then turn it on again to reset. Verify that the "overheat indicator" on the front of the temperature controller lights off.
Elevator overload detection	When the elevator load exceeds 50kg, it detects faults, and disables lifting operation (in such a case, the lifting switch ■ on the front of the instrument blinks red). When the measurement software is running, it exits automatically.	A reset switch for the elevator is located in the "temperature controller pocket" on the front of the instrument. After you remove the cause, press the reset switch to release any protective actions.
System faulty pressure detection (Only when the measurement software is started)	When any pressure gauge exceeds 130 kPa, it detects faults and triggers an emergency stop (exhaust process). Only in the adsorption/desorption measurement, it detects faults when P0 exceeds 110 kPa.	Leave it without any action until the software exhausting process is complete.
Turbo molecular pump overload detection (Only when the measurement software is started)	When air is sucked while the turbo molecular pump is in operation, it detects load and stops the TMP operation (in such a case, "TMP error" appears on the software screen).	Even when the TMP error is indicated, the measurement is not aborted. Stop the low-pressure measurement because vacuum is degraded. To stop measuring and reset the error, turn off the instrument power switch 10 minutes or more after the error detection, and turn it on again another 5 seconds later to reset.
Recovering from system error	In case measurement is stopped by some reason, urgent processing will begin at restart of the software.	When measurement is stopped, finish the software and restart it. Leave it as it is, since urgent processing will start automatically.

⚠ Do not shut off power to the main unit while the turbo molecule pump is in operation, or for 30 minutes after it stops. When power is removed during operation, or immediately after shutdown, the system pressure rises rapidly up to atmospheric pressure. It may apply overload to the turbo molecule pump, and accordingly it may cause failure.

ooo Startup and shutdown ooo

1. Startup of the BELSORP-max main unit

1. Turn on the power switch on the back of the main unit. The power indicator at the front of the main unit lights up.
2. Connect the rotary pump power cable to the AC outlet on the back of the instrument, and turn on the rotary pump.
3. When the instrument has not been used for a long time period, purge the instrument tubing according to “ooo Installing and replacing gas cylinders ooo, P. 90”.

⚠ Be sure to connect the rotary pump power cable to the “AC outlet”.

⚠ The Dewar vessel is made of glass. Careful attention is required for the handling.

⚠ It takes 5 hours for the pressure gauge used in the main unit to stabilize the pressure reading. Start measurement about 5 hours after power is supplied to the main unit.

2. Shutdown of the BELSORP-max main unit

In case using the instrument for the measurement, following turn-off procedure should be done more than 30 minutes after the measurement.

1. Turn off the power switch on the back of the main unit. The power indicator at the front of the main unit lights off.
2. Turn off the rotary pump immediately.
3. When the instrument will not be used for a month or more, close the gas main valve.

⚠ Caution

In case you turn off the pump first, turn off the instrument immediately.

- **When the instrument is still on after the rotary pump is turned off, oil may flow back into the instrument. This may contaminate the instrument with oil.**

Do not shut off power to the main unit while the turbo molecular pump is in operation, or for 30 minutes after it stops. When power is removed during operation, or immediately after the shutdown, the system pressure rises rapidly up to atmospheric pressure. It may apply overload to the turbo molecular pump, and accordingly it may cause failure.

- **Our company shall not be liable for any damage of the instrument caused by wrong operational procedures.**

Options

To meet various measurement requirements from customers, the following options are available with **BELSORP-max**. The software operations are common to all types of specifications; therefore, refer to ooo Basic software operation ooo on P. 83, and “Guidance support” on P. 90.

Model	Port No.	Pressure sensor in the sample section				Exhaust system
		1000 Torr	10 Torr	1 Torr	0.1 Torr	
Model 1 (0.1 Torr sensor)	1	○	△	−	△	TMP+RP (OP. DP) ＋WRG
	2	○	−	−	−	
	3	○	○	−	○	
Model 2 (1 Torr sensor)	1	○	−	△	−	TMP＋RP (OP. DP) ＋WRG
	2	○	−	−	−	
	3	○	−	○	−	
Model 3 (10 Torr sensor + TMP)	1	○	△	−	−	TMP＋RP (OP. DP) ＋WRG
	2	○	−	−	−	
	3	○	○	−	−	
Model 4 (10 Torr sensor)	1	○	△	−	−	RP＋ Pirani sensor
	2	○	−	−	−	
	3	○	○	−	−	

△ : selctable marker

※ For temperature device options, refer to P. 8.

※ For other optional equipment and oil-free exhaust system, refer to P. 9.

For details of the optional models, refer to the following pages.

ooo 1 Torr sensor specification ooo

This model is equipped with a 1 Torr sensor and a turbo molecular pump, and measures the adsorption isotherm in the range of $P/P_0 = 10^{-7}$ to 0.997. For other features, refer to "About BELSORP-max on P. 11".

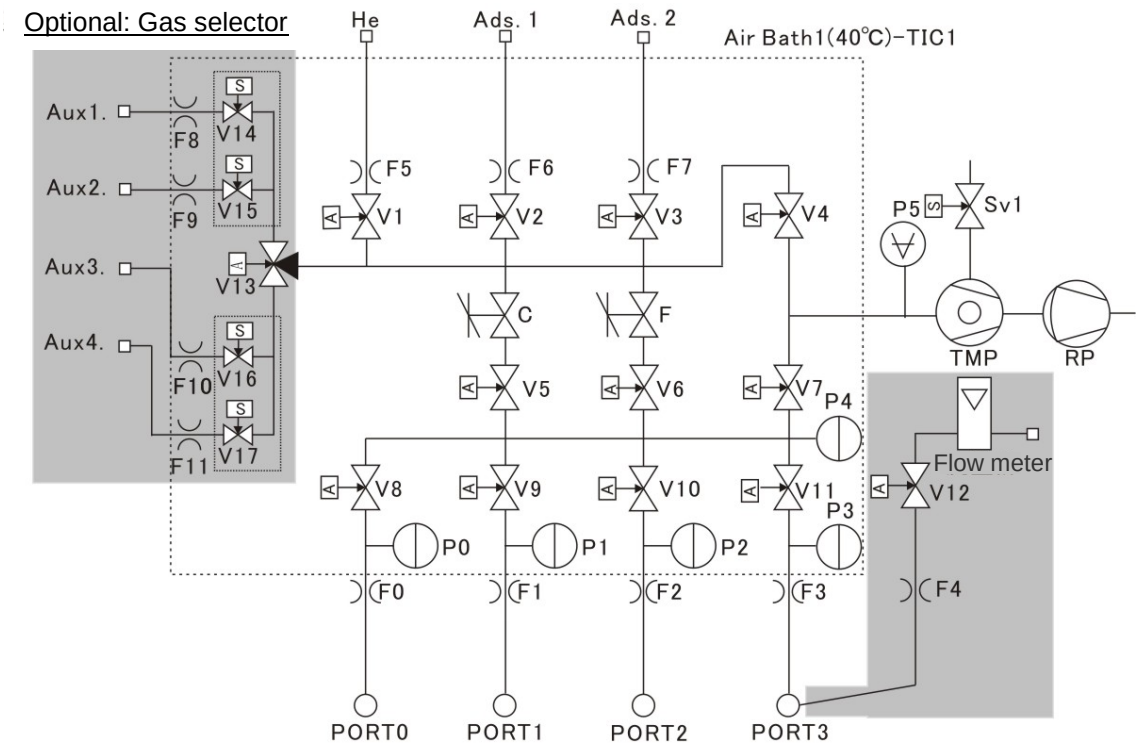
Model 2 (1 torr sensor) specification

Measurement method	Constant volume gas adsorption method+AFSM™	
Adsorptive	N_2, Ar, Kr, H_2, CO, O_2, CH_4, and other non-corrosive gas Steam (A corrosion resistant option is required for the adsorption measurement of corrosive gas such as NH_3 and amine, and organic vapor such as CH_3OH, C_6H_6, etc.)	
Number of samples to be measured	Standard mode ($P/P_0 = 10^{-7}$ to 0.997): 1 to 3 samples High precision mode ($P/P_0 = 10^{-7}$ to 0.997): 1 to 2 samples (according to AFSM™)	
Specific surface area measurement range [1)]	0.01 $m^2 g^{-1}$ or more (N_2 / 77K) 0.0005 $m^2 g^{-1}$ or more (Kr/77K)	
Pore size distribution (diameter)	0.35 to 500 nm	
Pressure sensor	133 kPa	5 units (Accuracy: ±0.25 % of F. S.)
	1.33 kPa	1 unit (Accuracy: ±0. 5 % of R.)
	133 Pa	1 unit (Accuracy: ±0.12 % of R) (OP. + 1 unit)
Pressure resolution	1.6×10^{-5} Pa	
Manifold temperature	40 °C (Option 50 °C)	
Dewar vessel	Volume: 2.6 L, Holding time: 60 h	
Sample cell	About 1.8 cm^3 (Optional: 5 cm^3)	
Exhaust system	Turbo molecular pump + Rotary pump : Attainable vacuum 6.7 x 10^{-7} Pa or less (manufacturer's specification) (Optional: Oil free exhaust system)	
Vacuum gauge	Cold cathode gauge (2 x 10^{-7} Pa to 1 Pa)	
Measurement software	Pretreatment and adsorption/desorption isotherm measurement	
Analysis program (BELMaster™)	・ Adsorption/desorption isotherm ・ Specific surface area by the Langmuir method ・ Pore volume calculation by the DA method ・ Micro-pore analysis by the MP method, HK method, and SF method ・ Diferece of adosorption method ・ Specific surface area by the BET method ・ Meso-pore size distribution by the DH, CI, BJH method ・ Micro-pore volume and micro-pore size analysis by the t-method and the α_S-method ・ Equivalent differential adsorption heat analysis ・ Pore size distribution analysis by the NLDFT/GCMC (BELSim™) (Optional)	

Required PC environment	OS: Windows 2000, XP, Vista, 7 CPU: Intel Processor Memory: 2 GB or more Hard disc: Free spaces of 1 GB or more USB port: USB 2.0
Auxiliary equipment	Rotary pump displacement: 50 L min^{-1} Attainable vacuum: 6.7 x 10^{-2} Pa
Utility	He, adsorptive (N_2, Ar, etc.) : 1/8" Swage lock joint (0.1MPa (gauge pressure)) Air for valve operation : 1/4" plastics tube quick connec(0.5 to 0.6MPa (gauge pressure)) Rotary pump connection port : NW16
Dimension / weight	W565 x H850 x D580 mm, 84 kg (Excluding a vacuum pump and computer related equipment)
Power	Single phase, AC100 to 240 V /800 VA (max. 700 VA for roughing vacuum pump)

1) The minimum specific surface area to be measured depends on the sample density.

Model 2 (1 Torr sensor) specification - main unit



①	V1 to V17	: Valve
②	C, F	: Flow rate adjustment needle valve
③	P0 to P4	: Pressure sensor
④	P5	: Vacuum gauge
⑤	TIC1	: Manifold temperature controller
⑥	Sv1	: Vent valve
⑦	TMP	: Turbo molecular pump

① Valve (Standard unit: V1 to 11)

V1 to 11: pneumatic valves

V1 : To dose helium gas

V2 : To dose the Ads. 1 gas

V3 : To dose the Ads. 2 gas or vapor

V4 : To exhaust the gas accumulator

V5 : To dose gas to the reference volume (large flow rate line)

V6 : To dose gas to the reference volume (small flow rate line)

V7 : To exhaust the reference volume

V8 : A valve between the P0 port and the reference volume

V9 : A valve between the measurement port 1 and the reference volume

V10 : A valve between the measurement port 2 and the reference volume

V11 : A valve between the measurement port 3 and the reference volume

Valve (optional)

Flow gas pretreatment line

A pneumatic valve

V12 : To be used in the flow gas pretreatment

Gas selector

V13: Pneumatic valve, V14 to V17: Solenoid valves

V13 : A valve between the gas selector and the gas accumulator

V14 : To dose the Aux. 1 gas

V15 : To dose the Aux. 2 gas

V16 : To dose the Aux. 3 gas

V17 : To dose the Aux. 4 gas

② Flow rate adjustment needle valve (C, F)

C : For large flow rate (pressure) control

F : For small flow rate (pressure) control

③ Pressure sensor (P0 to P4)

The following pressure gauges, with the indicated respective full scale, are installed to each port.

P0 : 133 kPa

To measure the pressure at the saturation vapor pressure measurement port (P0 port)

P1 : 133k Pa (Optional: 0.133kPa)

To measure the pressure at the measurement port 1

P2 : 133 kPa

To measure the pressure at the measurement port 2

P3 : 133 kPa, 0.133 kPa

To measure the pressure at the measurement port 3

P4 : 133 kPa, 1.33 kPa

To measure the pressure in the reference volume

Accuracy: 133 kPa → ±0.25 % (full scale)

: 1.33 kPa → ±0.5 % (reading)

: 0.133 kPa → ±0.12 % (reading)

④ Vacuum gauge (P5)

Cold cathode type pressure sensor

Measurement range: 2 x 10^{-7} Pa to 1 Pa

⚠ Do not use the vacuum gauge at pressure above 0.1 Pa.

⑤ Manifold temperature controller (TIC1)

Turn on the power switch on the back of the main unit, then the thermostatic manifold temperature is controlled to be 40°C (Option 50 °C). The manifold temperature is measured using a platinum temperature detector.

⑥ Vent valve (Sv1)

Turn off the circuit breaker on the back of the main unit, then this valve opens to vent the exhaust line to the open air to prevent the pump oil from flowing back to the instrument when the rotary pump is in operation.

⚠ Be sure to turn off the power switch and vent the exhaust line to the open air, before you shutdown the rotary pump. Otherwise, the pump oil may flow back to the main unit, and accordingly it may cause failure.

⑦ Turbo molecular pump (TMP)

Attainable vacuum: 6.7 x 10^{-7} Pa or below (manufacturer's specification)

It makes a high vacuum in the system.

⚠ Do not shut off power to the main unit while the turbo molecular pump is in operation, or for 30 minutes after it stops. When power is removed during the operation, or immediately after the shutdown, the system pressure rises rapidly up to atmospheric pressure. It may apply overload to the turbo molecular pump, and accordingly it may cause failure.

⚠ When accumulated operating time of the turbo molecular pump exceeds 20,000 hours, a maintenance work is prompted on the PC screen. Please contact our company if you find this message.

ooo 10 Torr sensor specification ooo

This model is equipped with a 10 Torr sensor and a 1000 Torr sensor, and performs the adsorption/desorption measurement in the range of $P/P_0 = 10^{-5}$ to 0.997. By installing an optional turbo molecular pump, it can perform the measurement at low pressure (Model 3 with a turbo molecular pump performs the measurement in the range of $P/P_0 = 10^{-6}$ to 0.997). For other features, refer to "About BELSORP-max on P. 11".

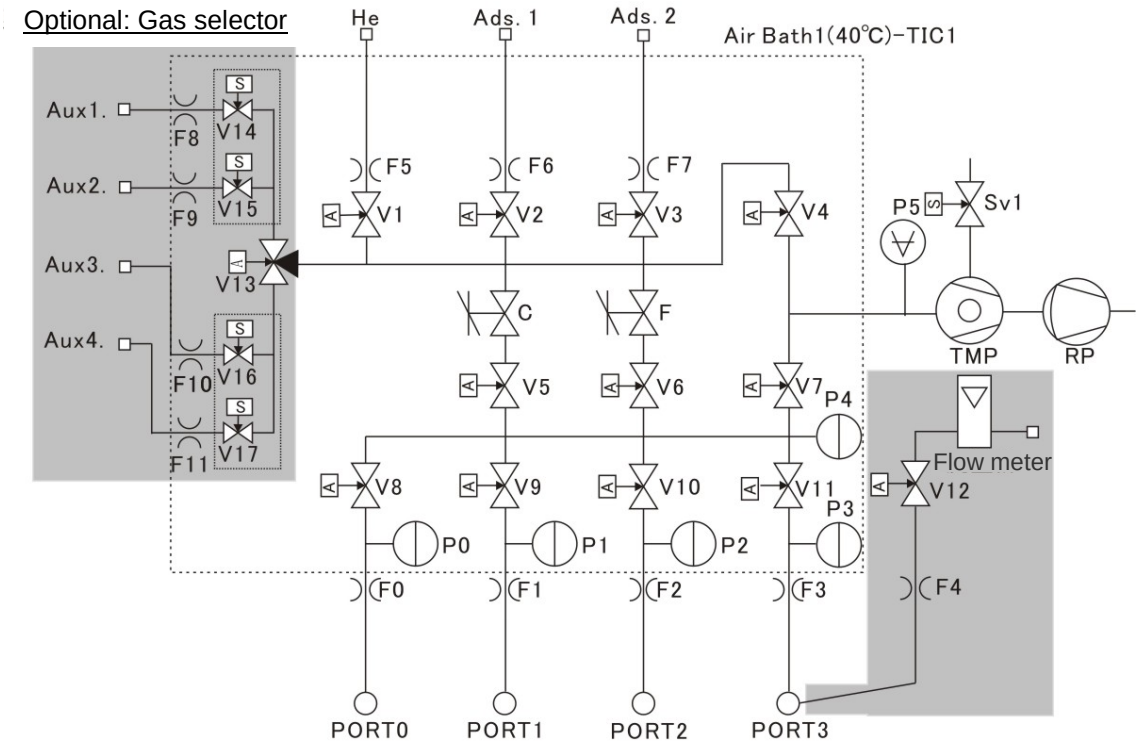
Model 3, 4 (10 Torr sensor) specification

Measurement method	Constant volume gas adsorption method+AFSM™	
Adsorptive	N_2, Ar, Kr, H_2, CO, O_2, CH_4, and other non-corrosive gas Steam (A corrosion resistant option is required for the adsorption measurement of corrosive gas such as NH_3 and amine, and organic vapor such as CH_3OH, C_6H_6, etc.)	
Number of samples to be measured	Standard mode ($P/P_0 = 10^{-5}$ to 0.997): 1 to 3 samples High precision mode ($P/P_0 = 10^{-5}$ to 0.997): 1 to 2 samples (according to AFSM™) In case of Model 3 + TMP: $P/P_0 = 10^{-6}$ to 0.997	
Specific surface area measurement range [1)]	0.01 $m^2 g^{-1}$ or more (N_2 / 77K) 0.0005 $m^2 g^{-1}$ or more (Kr/77K)	
Pore size distribution (diameter)	0.35 to 500 nm	
Pressure sensor	133 kPa	5 units (Accuracy: ±0.25 % of F. S.)
	1.33 kPa	1 unit (Accuracy: ±0. 5 % of R.)
Pressure resolution	1.6×10^{-5} Pa	
Manifold temperature	40 °C (Option 50 °C)	
Dewar vessel	Volume: 2.6 L, Holding time: 60 h	
Sample cell	About 1.8 cm^3 (Optional: 5 cm^3)	
Exhaust system	Rotary pump In case of Model 3 + TMP =: Attainable vacuum 6.7 x 10^{-7} Pa or less (manufacturer's specification) (Optional: Oil free exhaust system)	
Vacuum gauge	Pirani gauge (model3 Cold cathode gauge (2 x 10^{-7} Pa to atmospheric pressure)	
Measurement software	Pretreatment and adsorption/desorption isotherm measurement	

Analysis program (BELMaster™)	・ Adsorption/desorption isotherm ・ Specific surface area by the Langmuir method ・ Pore volume calculation by the DA method ・ Micro-pore analysis by the MP method, HK method, and SF method ・ Adsorption difference measurement ・ Specific surface area by the BET method ・ Meso-pore size distribution by the DH, CI, BJH method ・ Micro-pore volume and micro-pore size analysis by the t-method and the α_S-method ・ Equivalent differential adsorption heat analysis ・ Pore size distribution analysis by the NLDFT/GCMC (BELSim™) (Optional)
Required PC environment	OS: Windows 2000, XP, Vista, 7 CPU: Intel Processor Memory: 2 GB or more Hard disc: Free spaces of 1 GB or more USB port: USB 2.0
Auxiliary equipment	Rotary pump displacement: 50 L min^{-1} Attainable vacuum: 6.7 x 10^{-2} Pa
Utility	He, adsorptive (N_2, Ar, etc.) : 1/8" Swage lock joint (0.1MPa (gauge pressure)) Air for valve operation : 1/4" plastics tube quick connec(0.5 to 0.6MPa (gauge pressure)) Rotary pump connection port : NW16
Dimension / weight	W565 x H850 x D580 mm, 84 kg (Excluding a vacuum pump and computer related equipment)
Power	Single phase, AC100 to 240 V /800 VA (max. 700 VA for roughing vacuum pump)

1) The minimum specific surface area to be measured depends on the sample density

Model 3, 4 (10 Torr sensor) specification-unit



①	V1 to V17	: Valve
②	C, F	: Flow rate adjustment needle valve
③	P0 to P4	: Pressure sensor
④	P5	: Vacuum gauge
⑤	TIC1	: Manifold temperature controller
⑥	Sv1	: Vent valve
⑦	TMP	: Turbo molecular pump

① Valve (Standard unit: V1 to 11)

V1 to 11: pneumatic valves

V1 : To dose helium gas

V2 : To dose the Ads. 1 gas

V3 : To dose the Ads. 2 gas or vapor

V4 : To exhaust the gas accumulator

V5 : To dose gas to the reference volume (large flow rate line)

V6 : To dose gas to the reference volume (small flow rate line)

V7 : To exhaust the reference volume

V8 : A valve between the P0 port and the reference volume

V9 : A valve between the measurement port 1 and the reference volume

V10 : A valve between the measurement port 2 and the reference volume

V11 : A valve between the measurement port 3 and the reference volume

Valve (optional)

Flow gas pretreatment line

A pneumatic valve

V12 : To be used in the flow gas pretreatment

Gas selector

V13: Pneumatic valve, V14 to V17: Solenoid valves

V13 : A valve between the gas selector and the gas accumulator

V14 : To dose the Aux. 1 gas

V15 : To dose the Aux. 2 gas

V16 : To dose the Aux. 3 gas

V17 : To dose the Aux. 4 gas

② Flow rate adjustment needle valve (C, F)

C : For large flow rate (pressure) control

F : For small flow rate (pressure) control

③ Pressure sensor (P0 to P4)

The following pressure gauges, with the indicated respective full scale, are installed to each port.

P0 : 133 kPa

To measure the pressure at the saturation vapor pressure measurement port (P0 port)

P1 : 133k Pa (Optional: 1.33kPa)

To measure the pressure at the measurement port 1

P2 : 133 kPa

To measure the pressure at the measurement port 2

P3 : 133 kPa, 1.33 kPa

To measure the pressure at the measurement port 3

P4 : 133 kPa, 1.33 kPa

To measure the pressure in the reference volume

Accuracy: 133 kPa → ±0.25 % (full scale)

: 1.33 kPa → ±0.5 % (reading)

④ Vacuum gauge (P5)

Pirani gauge

Measurement range: 5 x 10^{-7} Pa to atmospheric pressure

(OP. cold cathode type pressure sensor Measurement range: 2 x 10^{-7} Pa to 1 Pa)

⚠ Do not use the vacuum gauge at pressure above 0.1 Pa.

⑤ Manifold temperature controller (TIC1)

Turn on the power switch on the back of the main unit, then the thermostatic manifold temperature is controlled to be 40°C (Option 50 °C). The manifold temperature is measured using a platinum temperature detector.

⑥ Vent valve (Sv1)

Turn off the circuit breaker on the back of the main unit, then this valve opens to vent the exhaust line to the open air to prevent the pump oil from flowing back to the instrument when the rotary pump is in operation.

⚠ Be sure to turn off the power switch and vent the exhaust line to the open air, before you shutdown the rotary pump. Otherwise, the pump oil may flow back to the main unit, and accordingly it may cause failure.

⑦ Turbo molecular pump (TMP)

Attainable vacuum: 6.7 x 10^{-7} Pa or below (manufacturer's specification)

It makes a high vacuum in the system.

⚠ Do not shut off power to the main unit while the turbo molecular pump is in operation, or for 30 minutes after it stops. When power is removed during the operation, or immediately after the shutdown, the system pressure rises rapidly up to atmospheric pressure. It may apply overload to the turbo molecular pump, and accordingly it may cause failure.

⚠ When accumulated operating time of the turbo molecular pump exceeds 20,000 hours, a maintenance work is prompted on the PC screen. Please contact our company if you find this message.

BELSORP-max measurement software

ooo System environment required ooo

This automatic gas adsorption measurement software is specialized for “BELSORP-max”.

It can be used in the following system environments. Standard BELSORP-max does not include a personal computer. You may use your personal computer.

<table>
<tr><th colspan="5">[Personal computer]</th></tr>
<tr><td></td><td colspan="4">Required system environment</td></tr>
<tr><td rowspan="2">Operating system</td><td>Microsoft Windows® 7 Home Basic or Home Premium or more</td><td>Microsoft Windows® Vista</td><td>Microsoft Windows® XP Home or Professional Edition</td><td>Microsoft Windows® 2000</td></tr>
<tr><td colspan="4">(Any computer that can run the English version of these OS)</td></tr>
<tr><td>CPU</td><td colspan="4">Intel processor</td></tr>
<tr><td>Memory</td><td colspan="2">2 GB or more</td><td>512 MB or more</td><td>256 MB or more</td></tr>
<tr><td>Display</td><td colspan="4">XGA (1024 × 768 dots) or more</td></tr>
<tr><td>Hard disk capacity</td><td colspan="4">10 GB or more space is required during operation.</td></tr>
<tr><td>USB port</td><td colspan="4">At least one USB1.1 / USB2.0 port</td></tr>
<tr><td>Disk drive</td><td colspan="4">CD-ROM drive
(For setup CD installation, and reading Config CD)</td></tr>
</table>

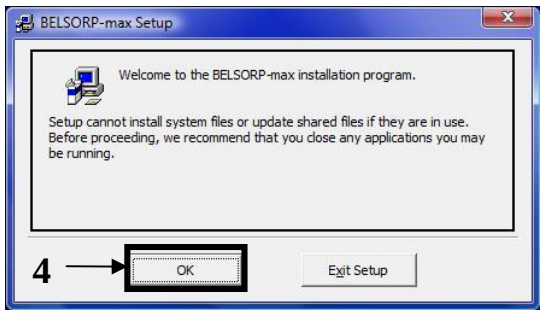
ooo Installing the software ooo

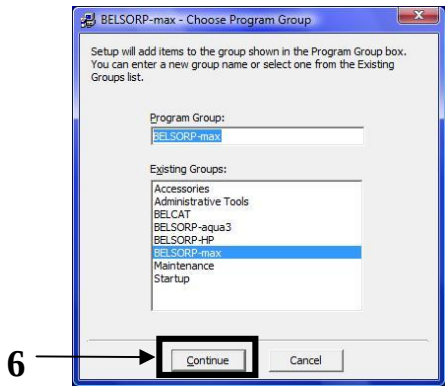
★ When measurement software has been already installed, delete the measurement software according to the "Uninstallation" in the next section before conducting the following installation procedure.

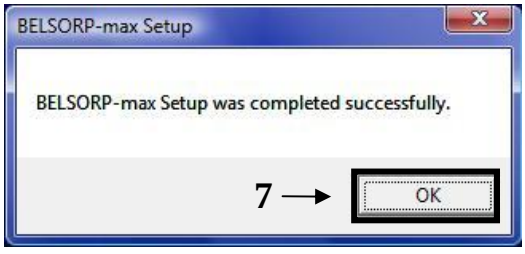
(For the basic operation of Windows, refer to the Windows instruction manual. The screens shown below are those in the Windows 7 mode.)

1. Installing the measurement software

1. Insert "Setup CD" to the CD-ROM drive.
2. Start "SETUP.EXE" in the "Measurement software ¥SETUP" folder stored in the "Setup CD".
3. After this is loaded, a screen appears as shown on the right.
4. Select the [OK] button.
5. Confirm the installation destination folder and then click the  button.
6. A screen appears as shown on the right.
   Select the [Continue] button to start setup.
7. When the setup is complete, a screen appears as shown below.
   Select the [OK] button.







2. Installing the USB driver

The main unit and the computer are connected using a USB cable. Install the USB driver according to the procedure described below.

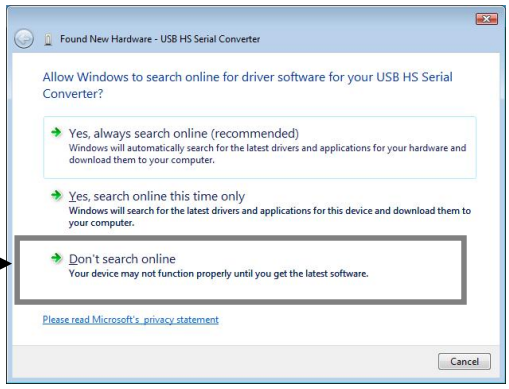
In the case of Windows® Vista

1. Turn on the main unit and the computer.

2. Connect the main unit to the computer using a USB cable.

3. A screen appears as shown on the right. Select "Locate and install driver software (recommended)".

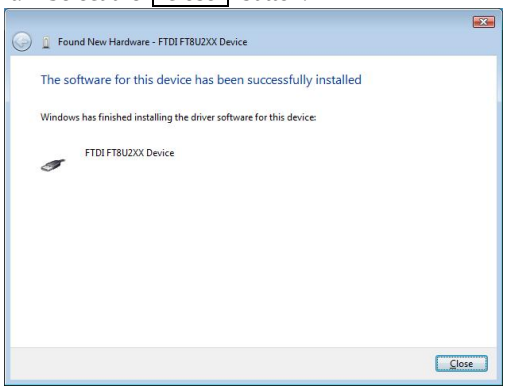
4. A screen appears as shown on the right. Select "Don't search online".



5. A screen appears as shown on the right. Insert "Setup CD" to the CD-ROM drive.

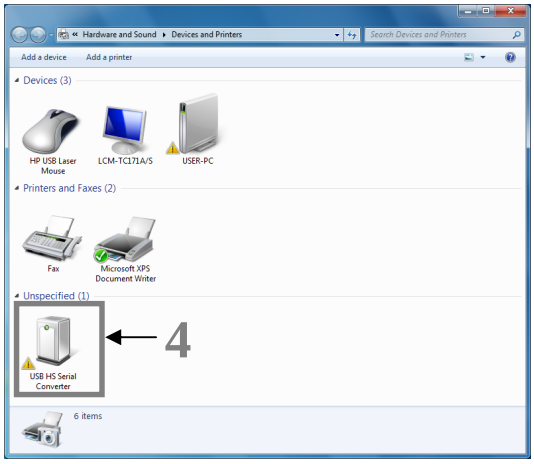
6. Select Next.

When the setup is complete, a screen appears as shown on the right. Select the close button.

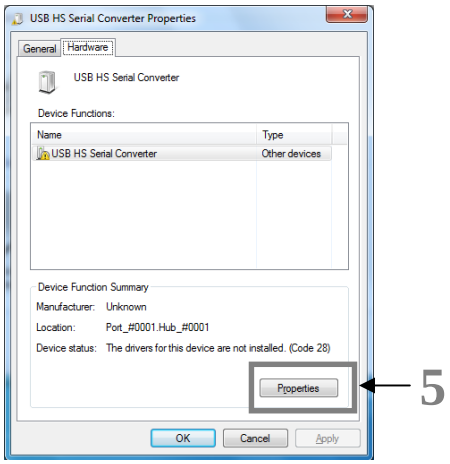


In the case of Windows® 7

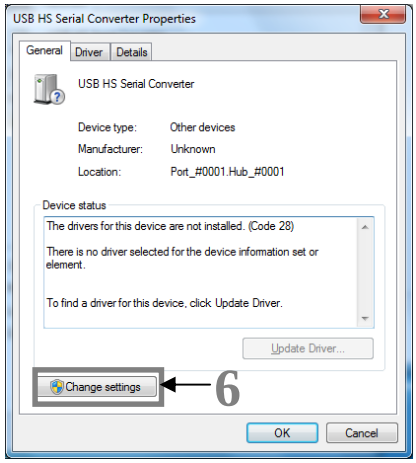
1. Turn on the main unit and the computer.
2. Connect the main unit to the computer using a USB cable.
3. Select Windows “Start” > “device and printa”
4. A screen appears as shown on the right. Righe click “USB HS Serial Converter”, and select “property”.



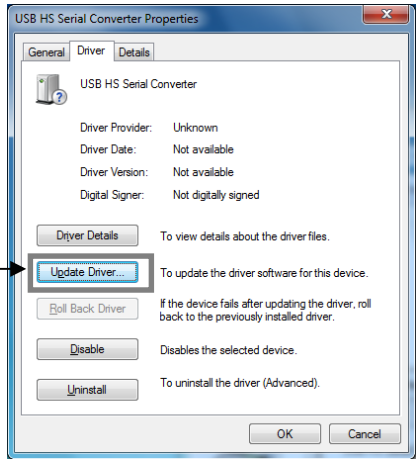
5. A screen appears as shown on the right. Select “property”.



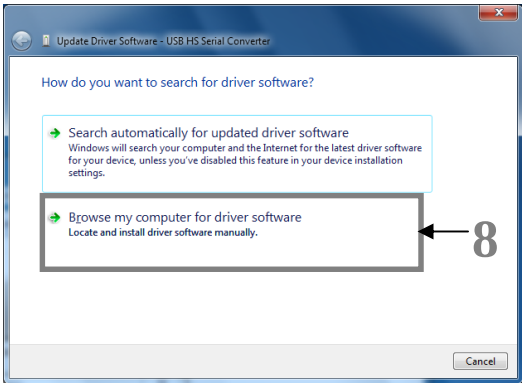
6. A screen appears as shown on the right. Select “change settings”.



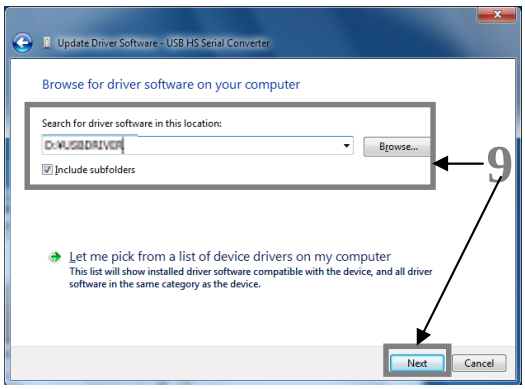
7. A screen appears as shown on the right. Select “updating driver”.



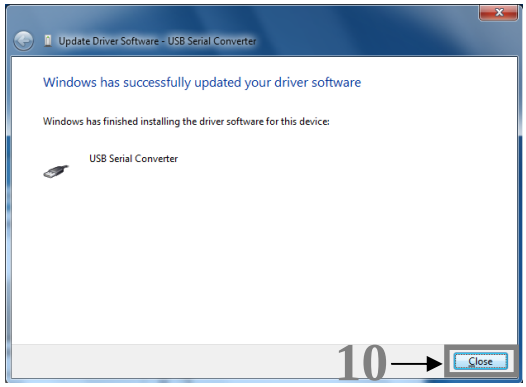
8. A screen appears as shown on the right. Select "Browse my computer for driver software".



9. A screen appears as shown on the right. Select "D: ¥USB DRIVER" in the "Setup CD", and select Next.



10. A screen appears as shown on the right. Select "close".



3. Copying the initial configuration file (Config. ini),(after Ver. 1.0.14)

1. The initial configuration file (Config. ini) contains various values specific to BELSORP-max, including the “reference volume”, etc. Copy these numeric data from the “Config CD” to the “SendDate” folder in the “BELmax” folder that has been already installed in section **1.** .

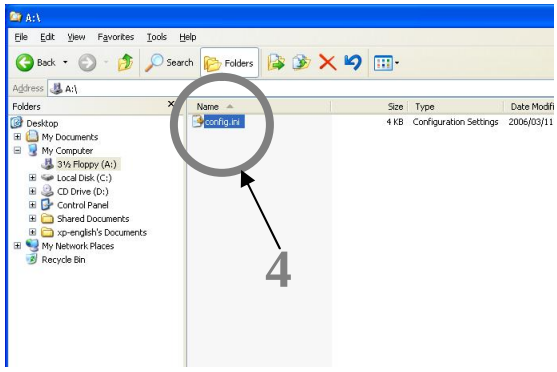
```
:**************************************************************************
:*                          Initial parameter file                        *
:**************************************************************************
:
:==========================================================================
:[Product name] BELSORP-max
:--------------------------------------------------------------------------
:[Last update] 2009/9/15
:==========================================================================
:
:------------------
:Instrument parameter
:------------------
        S/N             ="00001"        :Product serial No. [S/N]
        BELmax_type     =121            :Type 111, 121
                                        :     211, 212, 221, 222
                                        :     311, 321
:
        VS_0            =24.0000        :Standard volume (Vs[ml])
:
        FLOW_V12        =0              :Flow V12           (0=none, 1=yes)
        FLOW_V13_V17    =0              :Flow V13-17        (0=none, 1=yes)

        PUMP_KIND       =1              :0=RP,1=DF
:
:------------------
:RDA-016 Paramater
:------------------
        USB_SERIAL_NO   ="BELmax 00001"  :USB serial No. BELmax 00000
:
        AVE_COUNT       =40             :%

:------------------
```

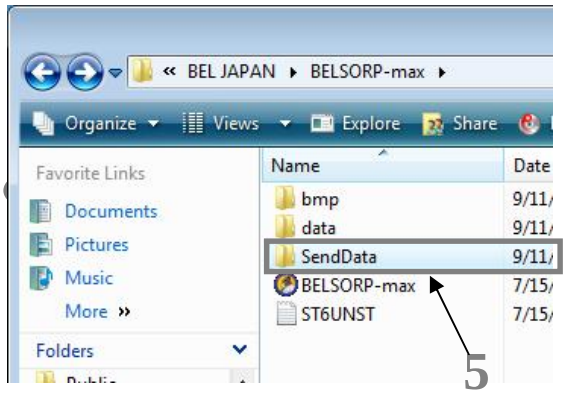
2. Insert the “Config CD” to the CD Drive (D:).

3. Select the Windows “Start” > “Program” > “Accessory” > “Explorer” to start “Explorer”.



4. Select the “Config. ini” file in the “CD Drive (D:)” folder, and Copy (C) it.

5. Paste (P) the “Config. ini” file to the “SendDate” folder in the folder that was created through “BELmax” or “**1.** Installing the measurement software – **5**”.



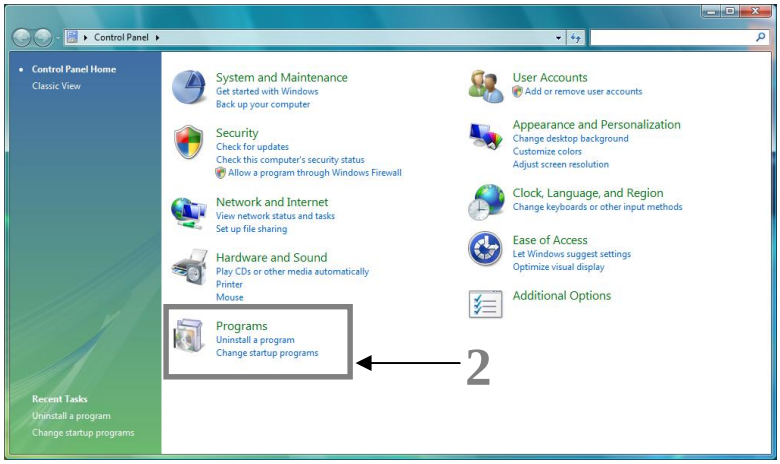
6. Exit “Explorer”. Now, the measurement software installation is complete.

ooo Uninstalling the software ooo

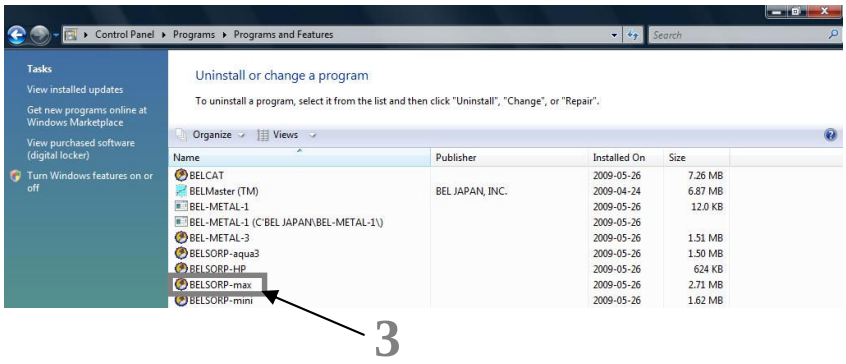
1. Uninstalling the measurement software

1. Select the Windows “Start” > “Control panel” to display the “Control panel” window.

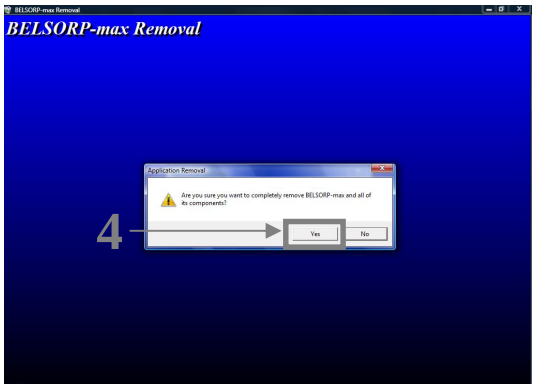
2. Start “Add or Remove Programs”.



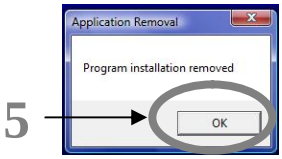
3. Select "BELmax" in the list.



4. Press the [Yes] button to start uninstallation.



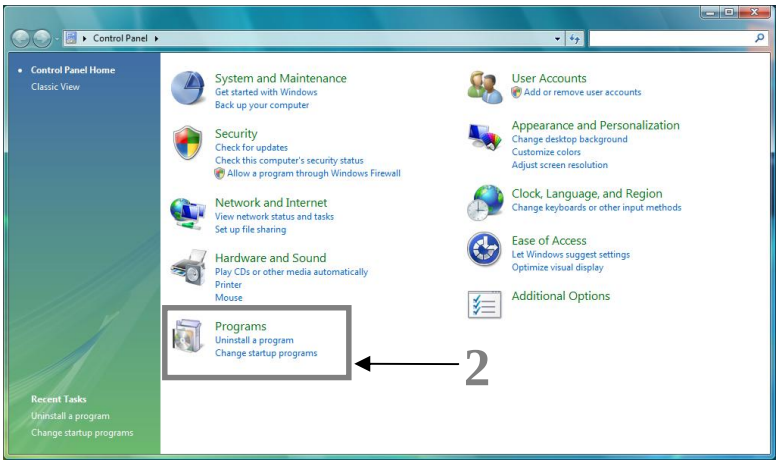
5. When the uninstallation is complete, a window appears as shown on the right. Press the [OK] button.



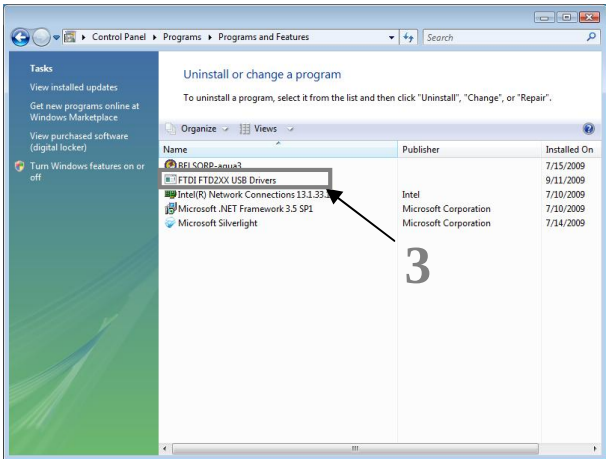
2. Uninstalling the USB driver

1. Select the Windows “Start” > “Control Panel” to display the “Control Panel” window.

2. Start “Add or Remove Programs”.

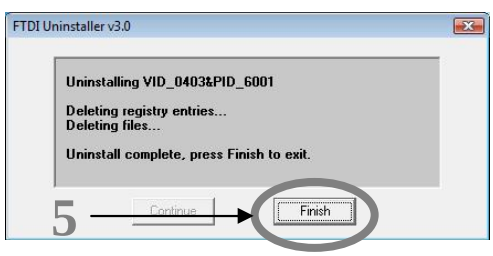


3. Select “FTDI FTD2XX USB Drivers” in the list of the applications installed, and select the “FTDI FTD2XX USB Drivers” button.



4. Press the Continue button to start uninstallation.

5. When the uninstallation is complete, a window appears as shown on the right. Press the Finish button. Now, uninstallation is complete.



ooo Basic software operation ooo

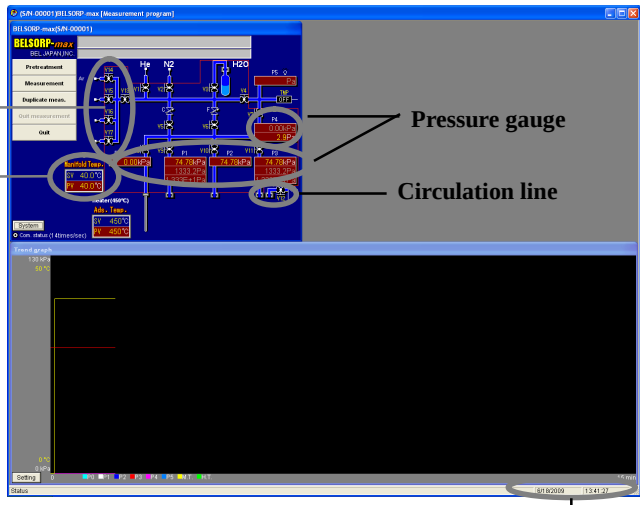
Starting the measurement software

1. Verify that the main unit and the computer are connected properly using a connection cable.
2. Check that power is supplied to the instrument.
3. Turn on the personal computer, and start “Windows”.
4. Select “Start” > “Program” menu > “BELmax” > “BELmax”.
5. The measurement software starts, and then the “Main” window appears. When the current status is displayed for the following items, startup is complete (The software screen shown below appears when you select the gas selector and the flow gas pretreatment line as options.).

- Current date and time
- Pressure gauge (P0-P4)
- Maniforld temperature (TIC1)

The following items are displayed when you select it as an option.

- Gas selector (V13 to V17)
- Circulation line (V12)



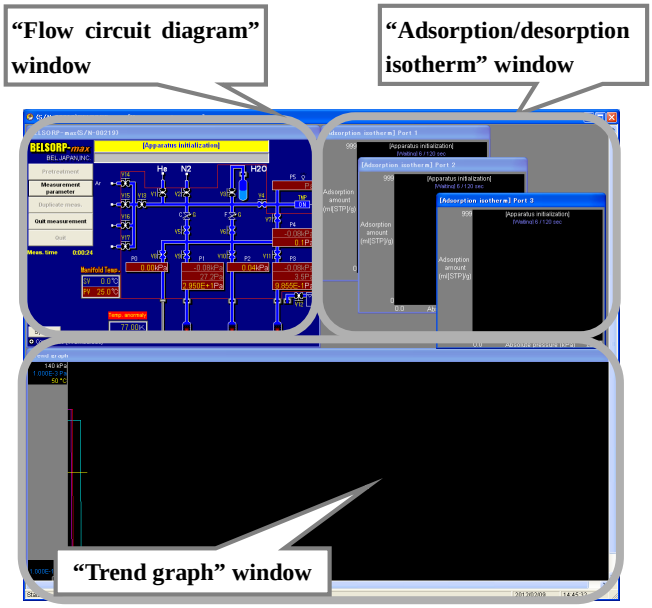
6. In the event of error in the communication line, including such cases that the main unit and the computer are not connected properly using a connection cable, etc. “Communication error” window is displayed. Check the power supply to the main unit, as well as connection of the power cable and the communication cable.

* If the valves (V1 to V17) still remain as opened manually when the software was used previously, all valves close when the software starts.

Operating the stop valves and specifying the temperature setting from the “Flow circuit diagram” window

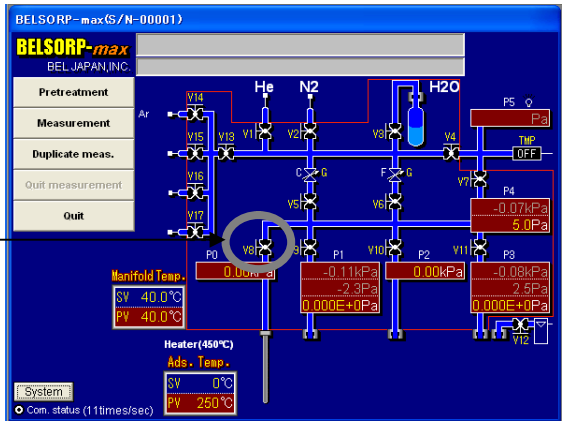
You can control the stop valves or change the temperature setting manually at any time; however, do not operate it during the automatic measurement.

The “Main” window of the measurement software (shown on the right) consists of the “Flow circuit diagram” window, the “Trend graph” window, and the “Adsorption/desorption isotherm” windows. The stop valves (V1 to V17) operation, vacuum gauges (P5), and turbo molecular pump (TMP) can be controlled from the “Flow circuit diagram” window, while the manifold temperature and adsorption temperature (when using a heater and electric furnace) can be specified from the same window.

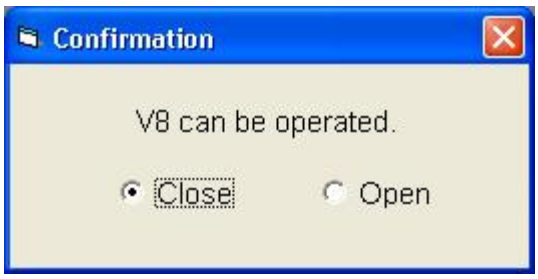


Operating the valves

1. On the “Flow circuit diagram” window, double-click the relevant mark of the valve (V1 to V17) to be operated.



2. Select “Close” or “Open” to operate the valve, and click the [X] button to close the “Confirmation” window.

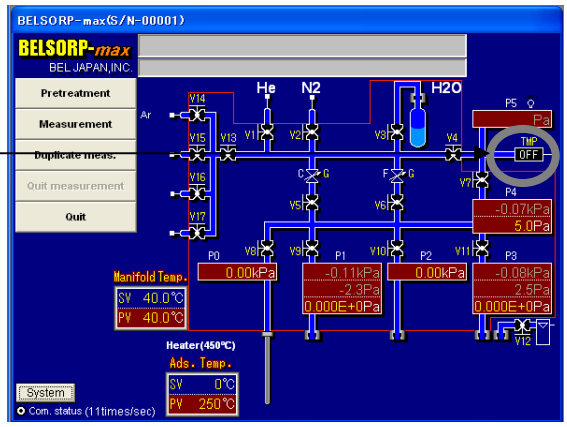


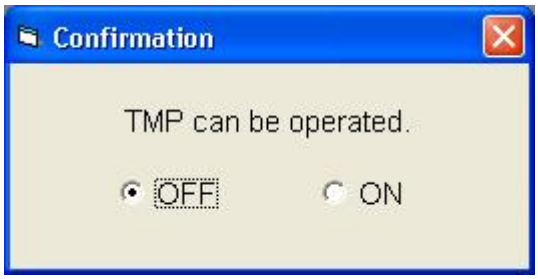
⚠ When you operate the valves manually, careful attention is required to prevent toxic/flammable gas from being discharged and to protect the turbo molecular pump from being overloaded.

Operating the turbo molecular pump

1. On the “Flow circuit diagram” window, double-click the ON or OFF mark of the TMP (turbo molecular pump).

2. Select OFF or ON, and use the × button to close the “TMP control” window. The TMP is controlled.

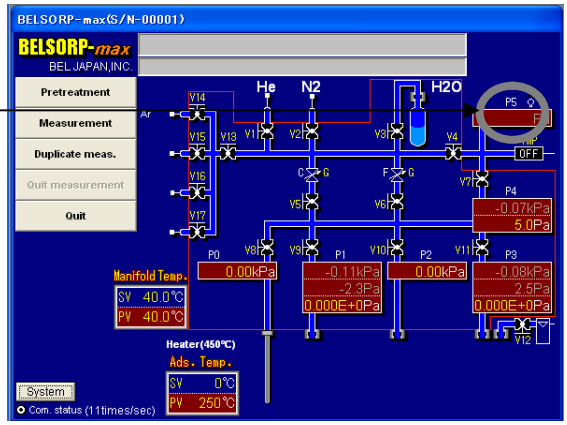




⚠ When you operate the turbo molecular pump manually, careful attention is required to prevent the turbo molecular pump from being overloaded.

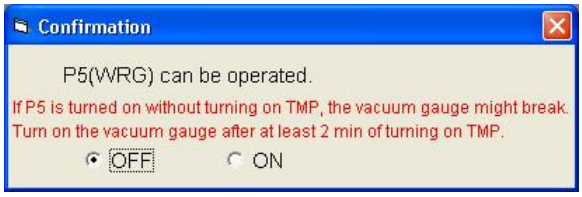
Operating the vacuum gauge P5 (WRG)

1. On the “Flow circuit diagram” window, double-click the lamp mark of the vacuum gauge P5 (WRG).



⚠ Do not turn on the WRG when the vacuum level is not sufficient. Otherwise, it may degrade filaments.

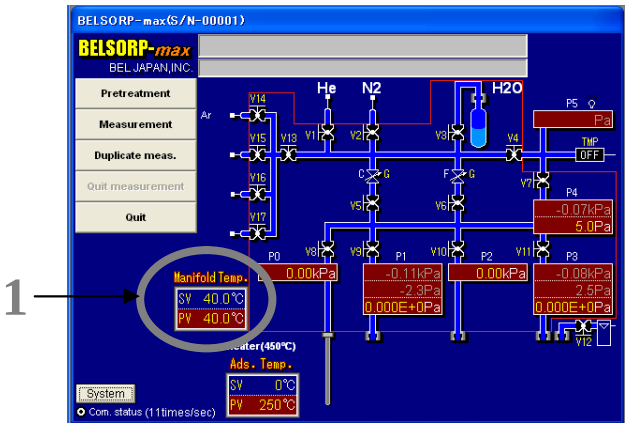
2. Select OFF or ON, and use the × button to close the “Confirmation” window. The vacuum gauge P5 (WRG) is controlled.



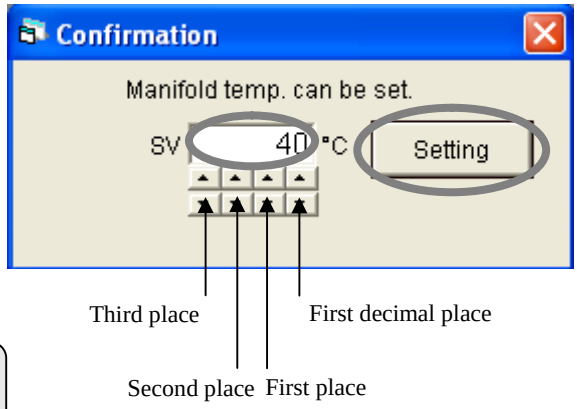
With 10 Torr (without TMP) specification, P5 is to be always displayed.

Operating the manifold temperature (Manifold Temp.)

1. On the “Flow circuit diagram” window, double-click the SV temperature indication of the manifold temperature (TIC1).



2. Enter the SV value (temperature setting), and select the Setting button. The SV value can be entered by using the ▲ (to increase), or ▼ (to decrease) button. Normally set it to 40 °C (Option 50 °C).



⚠ You may not specify any temperature above 40 °C(Option 50 °C).

Operating the measurement temperature (Heat Temp.)

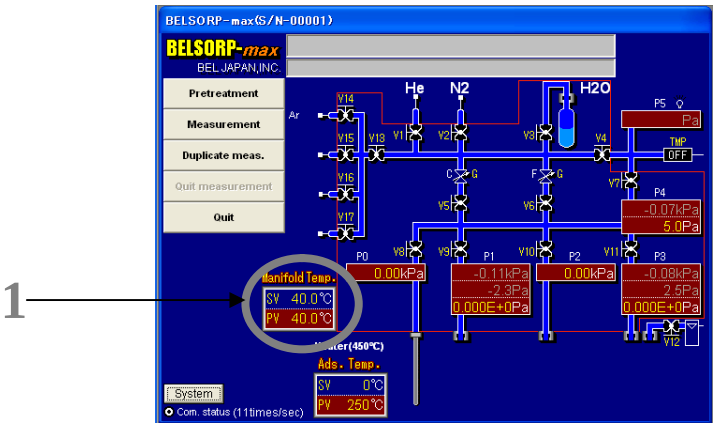
1. It can be operated when some temperature devices are connected, including a heater, electric furnace, and a temperature controller. On the “Flow circuit diagram” window, double-click the SV temperature indication of the adsorption temperature (TIC2). When any temperature device is not connected, the temperature indication is not displayed.

The temperature setting range is:

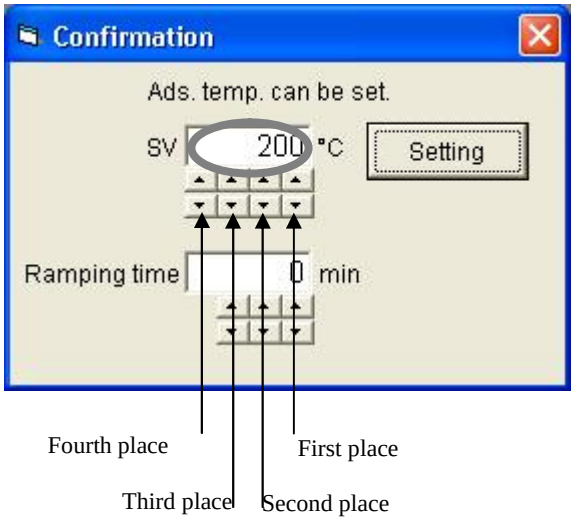
50 °C to 450 °C for the 450 °C heater,

50 °C to 550 °C for the 550 °C heater, and

50°C to 1100°C for the 1100 °C electric furnace.

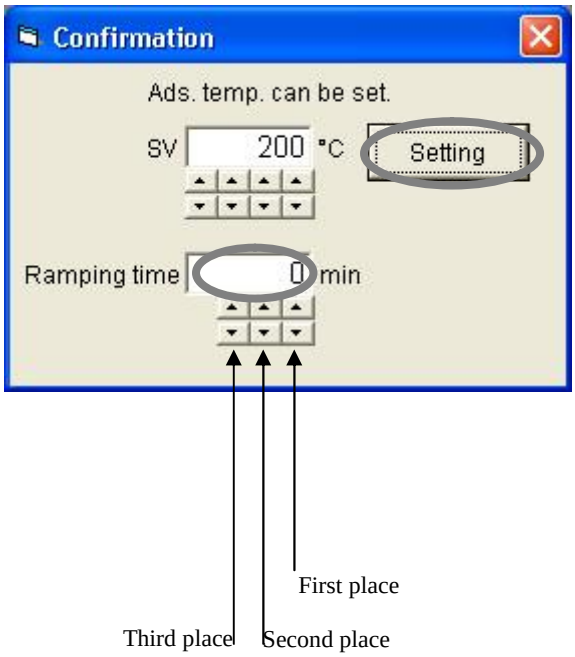


2. Enter the SV value (temperature setting). The SV value can be entered by using the ▲ (to increase), or ▼ (to decrease) button.



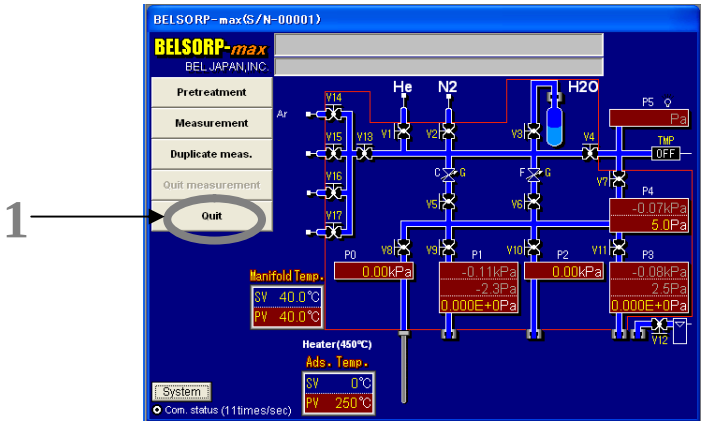
3. Enter the ramping time (minute). It can be entered by using the ▲ (to increase), or ▼ (to decrease) button. When the time setting is 1 minute or more, the temperature is controlled so that it changes from the initial PV value (current temperature) to the specified SV value in the time specified. In some cases, it cannot reach the target temperature in the time specified.

4. Select the Setting button. The adsorption temperature is controlled.

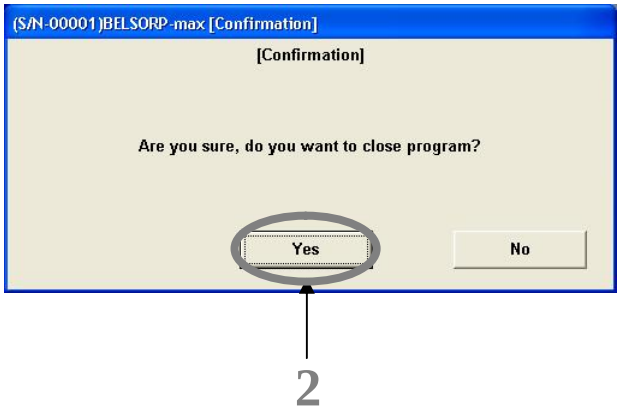


Exiting the measurement software

1. Select the Quit button, then the "Confirmation" window appears.



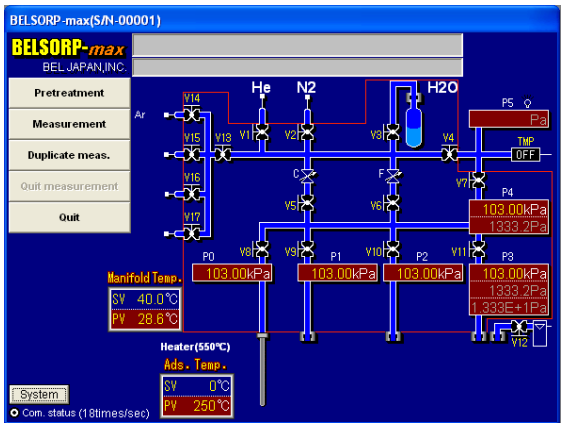
2. Select Yes to exit the measurement software. This software automatically closes all stop valves, and returns the instrument to the initial state.



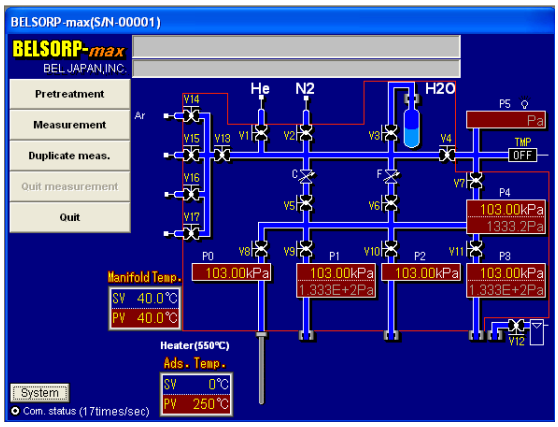
Software screen with optional specification

With 1 Torr, or 10 Torr sensor specification, the software screen appears as shown below (The basic software operation is the same as those with 0.1 Torr sensor specification).

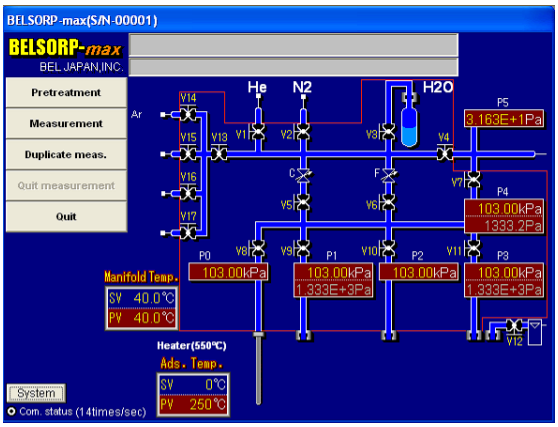
With 1 Torr specification



With 10 Torr specification (with TMP)



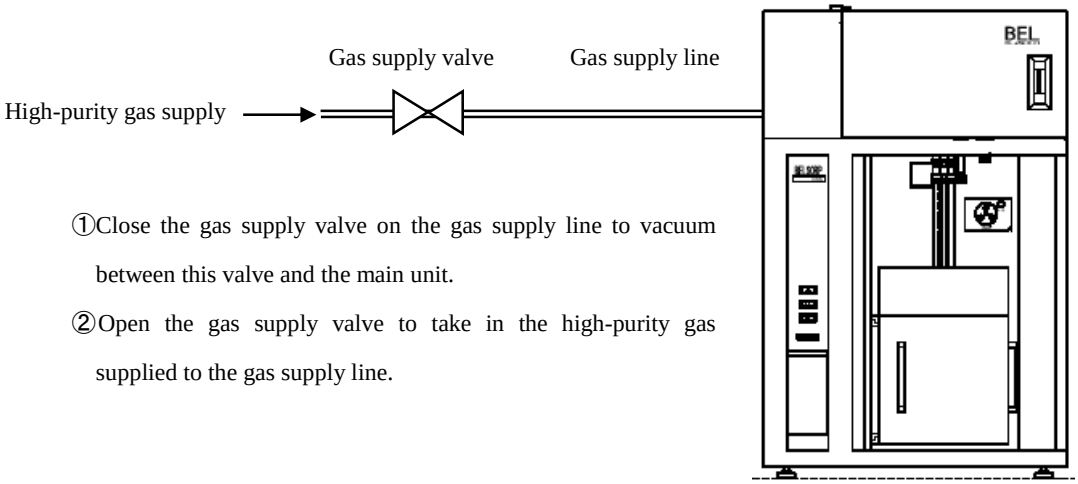
With 10 Torr specification (without TMP)



Guidance support

ooo Installing and replacing gas cylinders ooo

To measure adsorption/desorption correctly, a pure adsorptive gas and He gas are necessary. When a gas cylinder is replaced, air comes into the tube, so that gas purity in the gas supply line is degraded. Hence, it is necessary to wash the tube and fill in the gas supply line with a high-purity gas. The outline of tube washing is as follows:



①Close the gas supply valve on the gas supply line to vacuum between this valve and the main unit.

②Open the gas supply valve to take in the high-purity gas supplied to the gas supply line.

Fill in the gas supply line with the high-purity gas only by repeating the steps ① to ②.

BELSORP-max's measurement software is equipped with a guidance function to ensure easy operation when a gas pipe is attached for changing adsorptive gas or replacing the gas cylinder. The procedure to perform work by following this guidance is described from the next page. In this procedure, a gas cylinder is used as the gas source. Even when using other gas sources such as centralized line, wash the gas line in accordance with the following procedure. When you wash two or more different gas lines, be sure to perform it one by one.

The section of pipe washing by the software guidance function describes the case in which the regulat or mentioned on the next page is used. Change the operational method according to your regulator

Caution

Do not apply pressure more than 0.2 MPa (2 kgf cm^{-2}).

- **Otherwise, gas may flow back in the system, and accordingly the pressure sensor may be damaged.**

Do not use any corrosive gas (except for the corrosion resistant type).

Check the gas line for leakage, and verify that there is no leak.

Prevent any flammable gas or toxic gas from being discharged. Conduct abatement where applicable.

Make an appropriate arrangement for the pump exhaust port.

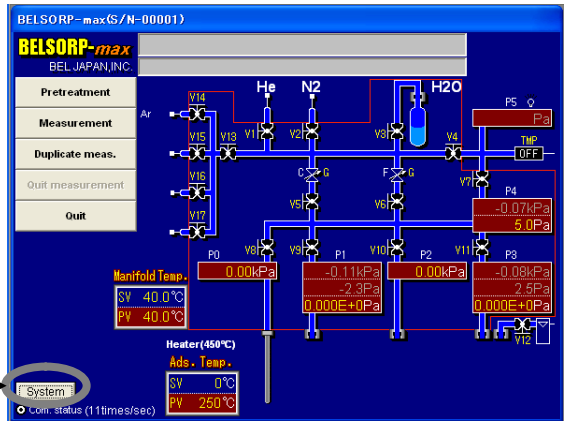
- **Particular attention is required in handling flammable gas, or toxic gas.**

Attention is required in using gas cylinders and compressed gas.

1. Connect the gas line between a gas cylinder and the **BELSORP-max** main unit. Check the line for leakage after it is connected.

2. Start the **BELSORP-max** measurement software. Close all valves when the software has been already started and valves are open.

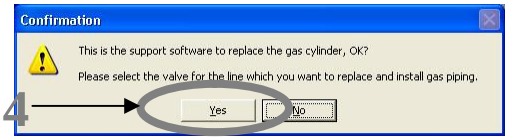
Press the System but ton at the lower left on the "Flow circuit diagram" window.



3. A window appears as shown on the right.

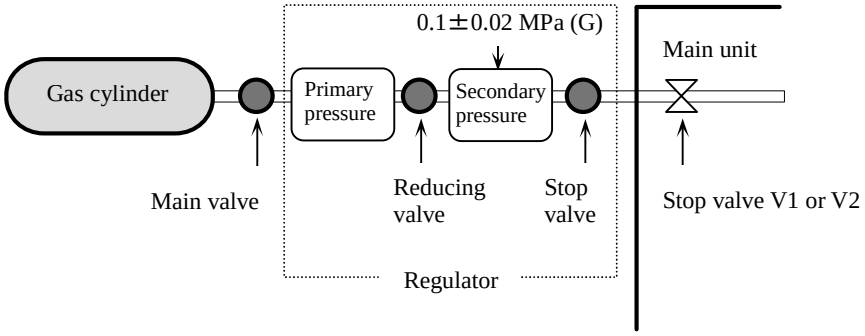
Select Exchanging gas cylinder.

4. When the "Confirmation" window is displayed, select Yes. In the next step **5** and later, follow the guidance message displayed on the "Confirmation" window.

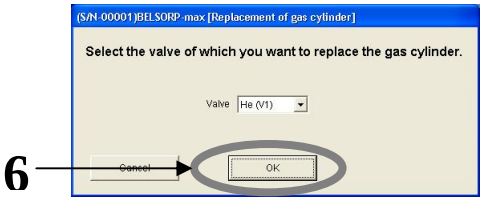


5. The terminology used in the "Confirmation" window is as follows.

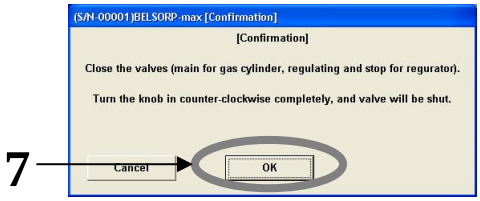
Main valve	A manual valve attached to a gas cylinder.
Reducing valve	A valve attached to a regulator for adjusting the secondary pressure.
Stop valve	A valve attached to a regulator. Gas is discharged when it opens.
Gas accumulator	A part of tubing in the main unit.



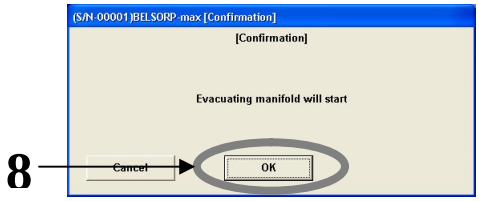
6. Select the valve of which gas cylinder you want to replace. After it is selected, press the OK button. For the adsorptive gas assignment to each valve, refer to the "Measurement parameter setting, Gas dosing valve assignment settings on P. 134".



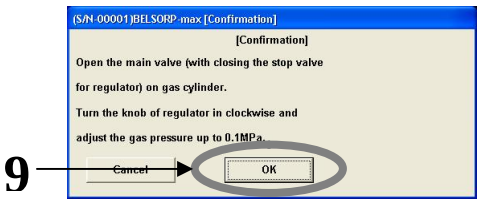
7. Close the gas cylinder main valve, the regulator stop -valve and the regulator reducing-valve; and then press the OK button.



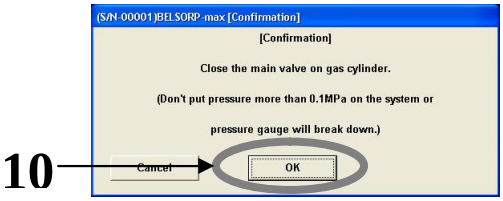
8. When a message is displayed as shown on the right, press the OK button. Firstly, air in the connection line is drawn into the system gas accumulator, and then discharged.



9. When a message is displayed a little while later as shown on the right, follow the message guidance, and then press the OK button to proceed to the next step.

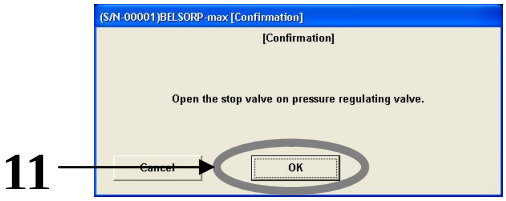


10. When a message is displayed as shown on the right, close the gas cylinder main valve, and then press the OK button to proceed to the next step.

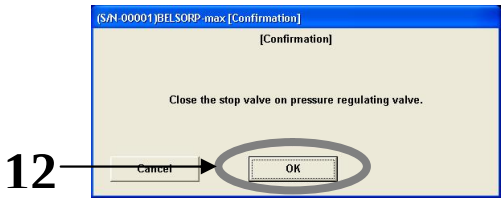


> Do not apply any pressure over 0.1 Mpa (G). The pressure sensor may be damaged.

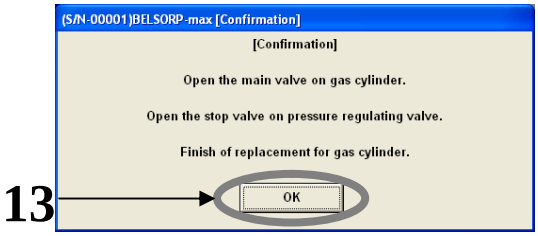
11. When a message is displayed as shown on the right, open the regulator stop valve, and then press the OK button to proceed to the next step. The helium gas accumulated in the regulator in steps **9.** and **10.** is released into the system, and then discharged (for washing inside the regulator).



12. When a message is displayed a little while later as shown on the right, close the regulator stop valve, and then press the OK button to proceed to the next step. Return to **9.,** and repeat the steps **9.** to **12.** two more times, i.e. a total of 3 times.



13. When a window appears as shown on the right, the gas cylinder replacement is complete. Finally, open the gas cylinder main valve and the regulator stop valve. Press the OK button to complete.



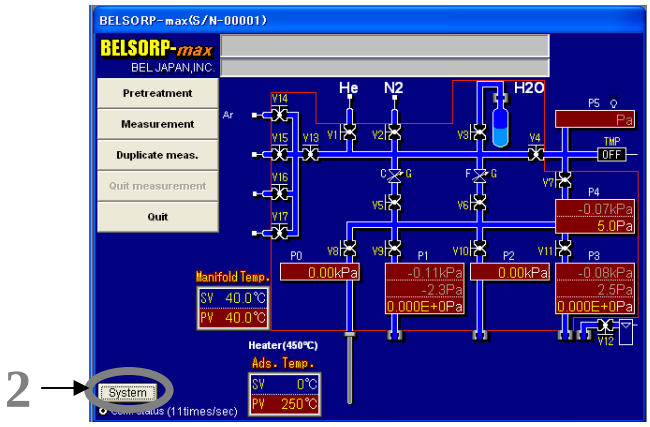
- Be sure to open the main valve and the stop valve at the end. Otherwise, any measurement cannot be performed with the valve closed.
- Verify that the regulator secondary pressure is 0.1 ± 0.02 MPa (G) after the replacement. In the automatic measurement and the “system check” described later, the regulator secondary pressure should be within the range mentioned above.

ooo System check ooo

Although individual devices are adjusted and inspected sufficiently before delivery, regulator needle valves for gas flow rate adjustment may be misadjusted during transportation. The “system check” function is used to check easily the regulator needle valve adjustment, the pressure sensor operation, and the valve operation. Any faults in the instrument may not only affect the measurement data accuracy, but also result in failure of the instrument. After the unit is installed or transferred, or when the unit has not been used for a long time period, be sure to perform this “system check”.

⚠ Do not install the sample cell to the measurement port, until it is prompted.

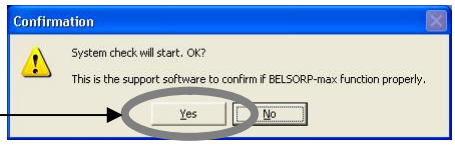
1. Start the BELSORP-max main unit and the measurement software.
2. Select the System button on the “Flow circuit diagram” window. The “System version information” window appears.



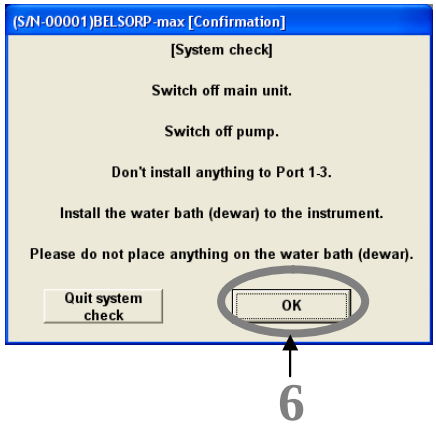
3. The system checks for the needle valve flow rate, valve operation, pressure sensor, Dewar vessel lifting operation, vacuum level, leakage, etc.. Remove the sample cells from Port 1 to 3 before you start the system check.

4. Select the System check… buttonon the “System version information” window.

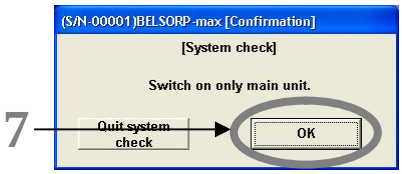
5. Select [Yes] to start the "System check".



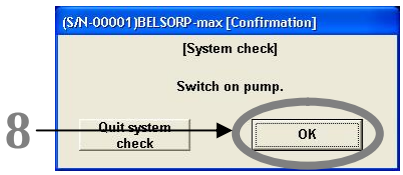
6. The system depressurizes the line between the main unit and the pump down to atmospheric pressure. When a window is displayed as shown on the right, turn off the main unit. Also, turn off the pump.



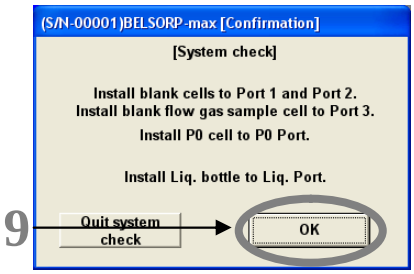
7. When a window is displayed as shown on the right, turn on the main unit only. Press the [OK] button.



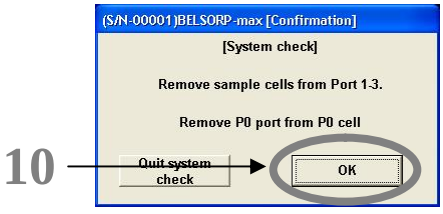
8. When a window is displayed as shown on the right, turn on the pump. Press the [OK] button.



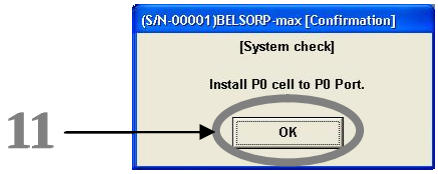
9. When a window is displayed as shown on the right, install blank sample cells to Port 1 to 2, a blank flow gas sample cell Port 3, a saturation vapor pressure reference cell to P0 port, and a liq. bottle to the adsorptive gas dosing port (ads.2), and then press the [OK] button. When the flow gas pretreatment line is equipped, install a blank flow gas sample cell to Port 3.



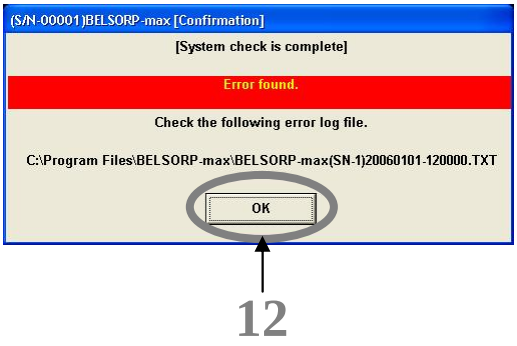
10. A window is displayed as shown on the right after the leak check. Remove the sample cells from Port 1 to 3, and the saturation vapor pressure reference cell from P0 port, and then press the [OK] button.



11. A window is displayed as shown on the right after you adjust the needle valves V5 and V6 flow rate. Install a saturation vapor pressure reference cell to P0 port, and press the OK button.



12. When the system check is not successfully complete, a window is displayed as shown on the right. Check the error log file. Press the OK to close the window.

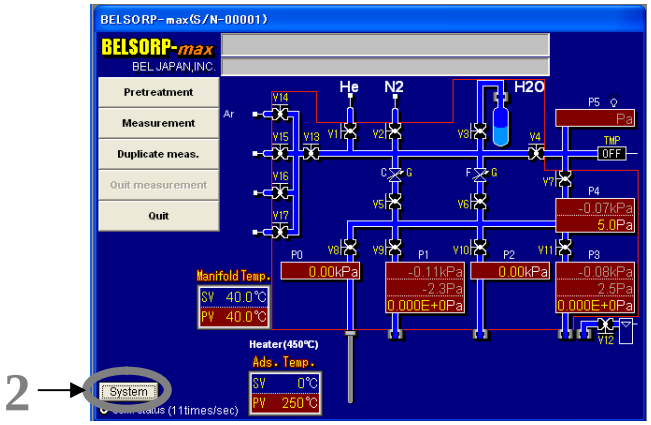


ooo Adjusting the needle valve ooo

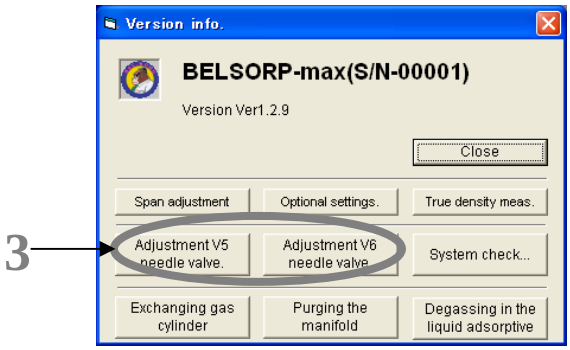
Adjust the needle valve to the appropriate flow rate.

	Function
Adjustment V5 needle valve	Check the flow rate through the needle valve V5 (C) for a large flow rate. Select this button to check the flow rate through the needle valve V5 (C). Adjust the needle valve V5 (C) so that it takes 20 to 30 seconds to dose helium gas up to 100 kPa. For the vapor measurement, adjust the needle valve V5 (C) so that it takes 7 to 10 seconds to dose helium gas up to 100 kPa.
Adjustment V6 needle valve	Check the flow rate through the needle valve V6 (F) for a small flow rate. Select this button to check the flow rate through the needle valve V6 (F). Adjust the needle valve V6 (F) so that it takes 20 to 30 seconds to dose helium gas up to 1 kPa. For the vapor measurement, adjust the needle valve V6 (F) so that it takes 80 to 100 seconds to dose helium gas up to 100 kPa.

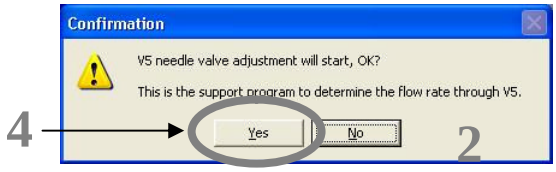
1. Start the **BELSORP-max** main unit and the measurement software.
2. Press the System button on the "Flow circuit diagram" window. The "System version information" window appears.



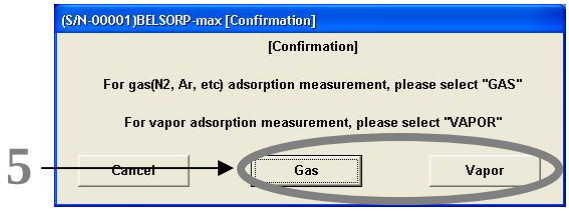
3. Select "Adjustment V5 needle valve" (or V6) on the "System version information" window.



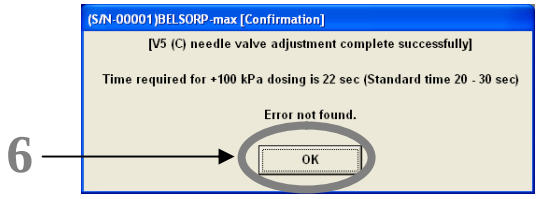
4. Select Yes.



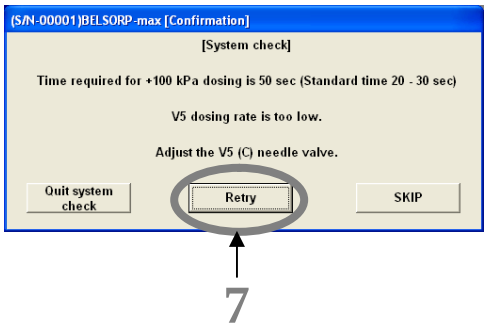
5. Select Gas for gas adsorption measurement, or select Vapor for vapor adsorption measurement. Then, start dosing helium gas to the reference volume buffer to determine the gas flow rate through the needle valve V5 (C) or V6 (F).



6. When the valve flow rate is appropriate, a window is displayed as shown on the right. Press the OK button.



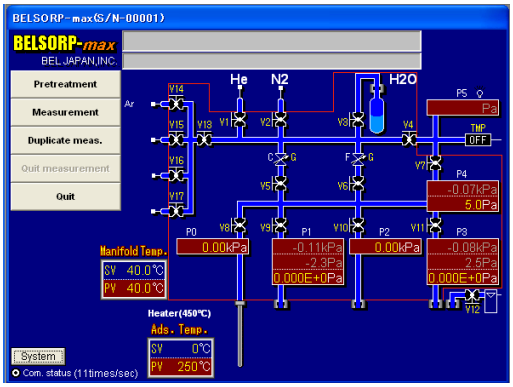
7. When the valve flow rate is not appropriate, a window is displayed as shown on the right. Select Retry to adjust it again.



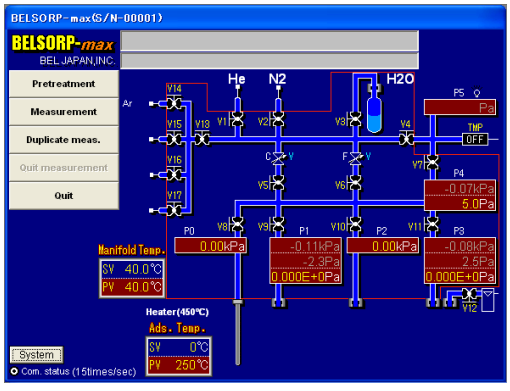
8. You can locate the “needle valve adjustment screw” in the back of the main unit measurement port. Adjust it by hand. Turn it counterclockwise to close the valve so that flow rate is decreased, or turn it clockwise to open the valve so that the flow rate is increased.

9. You can check adjustment of the needle valve is either gas (G) or vapor (V) in the flowchart.

【Setting gas (G)】



【Setting vapor (V)】



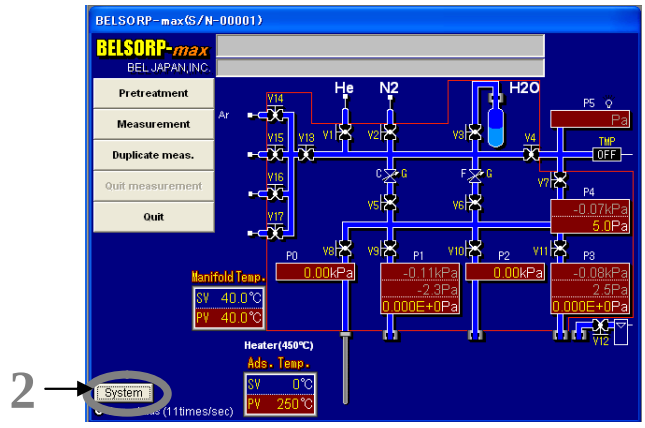
ooo Span adjustment ooo

The span adjustment is to prevent each pressure gauge from deviating, and to adjust it so that good balance is maintained. Perform this span adjustment when the instrument is installed, or the instrument has not been used for a long time period, or the pressure gauges deviate from each other. It is recommended to perform this span adjustment every time you perform the measurement at low pressure, or the low specific surface area measurement, the vapor measurement.

> ⚠ It is recommended to perform this span adjustment every time you perform the measurement at low pressure, or the low specific surface area measurement, the vapor measurement.

1. Start the BELSORP-max main unit and the measurement software.

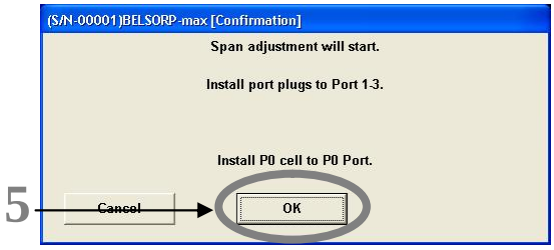
2. Press the System button on the "Flow circuit diagram" window. The "System version information" window appears.



3. Select the Span adjustment button.

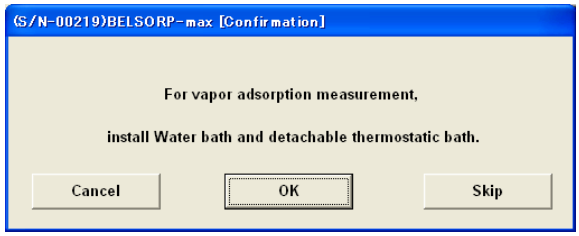
4. Select Yes to start the "span adjustment".

5. Install the port plugs to Port 1 to 3, install a saturation vapor pressure cell to P0 port, and then press the OK button. The span adjustment starts.

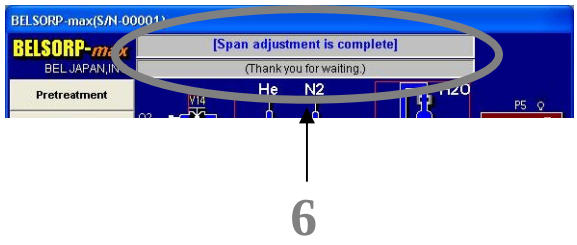


6. For vapor adsorption measurement, press the OK button.

For other adsorption measurement, choice Skip button.



7. When a message is indicated as shown on the right, the span adjustment is complete.



ooo Purging the tubing in the instrument ooo

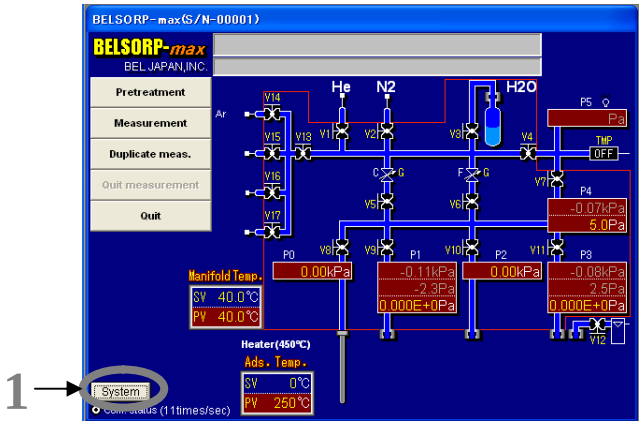
After the adsorptive is changed, the adsorptive previously used may still remain in the instrument tubing. This affects the subsequent measurement accuracy. When the instrument has not been used for a long time period such as more than two weeks, air and/or moisture may be contained in the instrument tubing. Additionally perform a purge each time a measurement is finished if a corrosive gas or a gas oxidizing in air (e.g. NO) is used. In such cases, you must purge the instrument tubing. With **BELSORP-max**, the measurement software has a guidance function to make this purging process easy. The following section describes the working procedure according to the guidance.

Caution

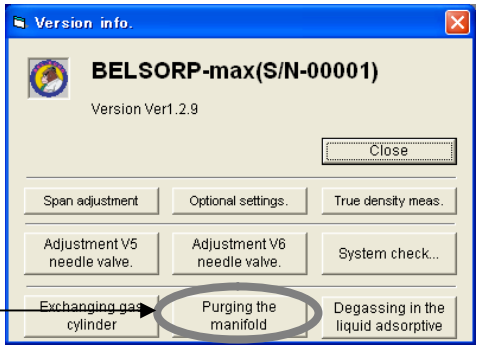
Install a helium gas cylinder before you attempt this work.

- **Use helium gas for purging.**

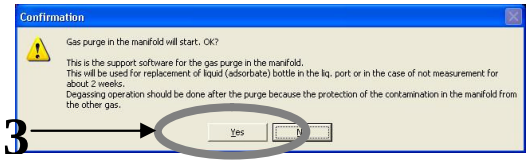
1. Start the **BELSORP-max** measurement software. Close all valves when the software has been already started and valves are open. Press the System button at the lower left on the "Flow circuit diagram" window.



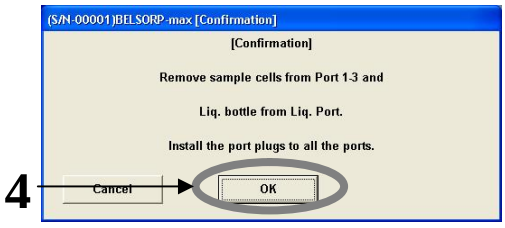
2. A window appears as shown on the right. Select Purging the manifold.



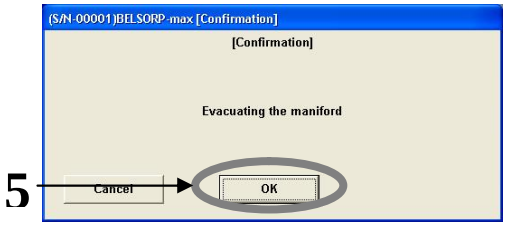
3. When the "Confirmation" window is displayed, select Yes. In the following step **4** and later, follow the guidance messages displayed on the "Confirmation" window.



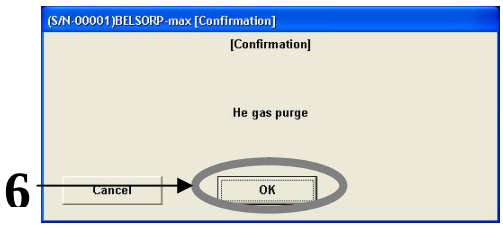
4. Remove the sample cell and the liq. bottle from the instrument, and install port plugs alternatively. When this is complete, press the OK button to proceed to the next step.



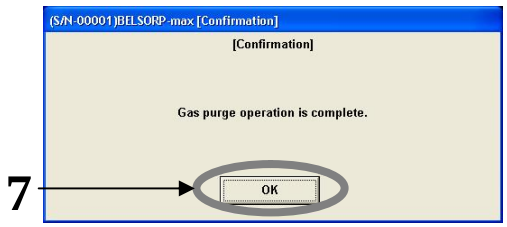
5. When a message is displayed as shown on the right, press the OK button to proceed to the next step. The whole instrument tubing is evacuated automatically for about 3 minutes.



6. A message will be displayed about 3 minutes later as shown on the right. Press the OK button to proceed to the next step. The main unit fills the whole instrument tubing with helium gas, and then discharges it. This purging process is repeated 3 times automatically.



7. When a window appears as shown on the right, the purging process is complete. Press the OK button.



ooo Degassing from adsorbate ooo

When you perform measurement using vapor gas as an adsorptive by installing a liq. bottle to the dosing gas port (ads. 2) (available only when the optional water bath is selected), you must remove the gas other than the adsorptive that is remaining in the liq. bottle and in the tubing between the valve V3 and the liq. bottle, and the gas dissolved in the adsorbate (liquid). When the instrument has not been used for a long time period such as more than a month, air and/or moisture may be contained in the liq. bottle or the tubing. In such cases, perform "degassing from adsorbate" according to the following procedure. With BELSORP-max, the measurement software has a guidance function to make degassing easy. The following section describes the working procedure according to the guidance.

Caution

Keep the adsorptive liquid level lower than 70 % of the liq. bottle.

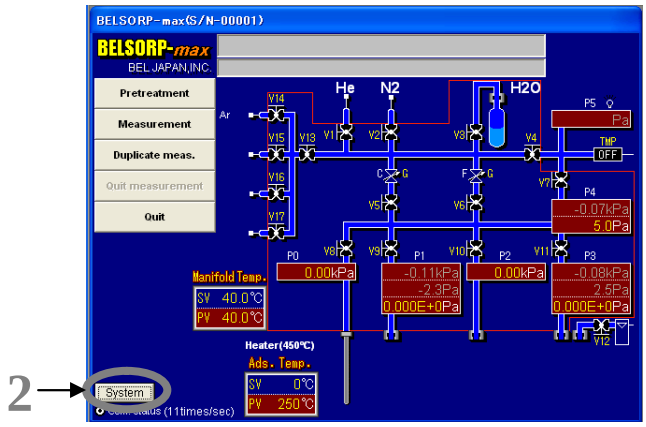
- **Otherwise, the liq. bottle may be broken during the degassing process.**

Careful attention is required in handling liquid nitrogen.

1. Wash the liq. bottle and dry it sufficiently.

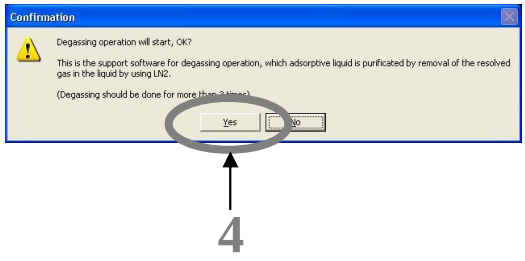
Be sure to wash the bottle with pure water, and then dry it sufficiently. Unclearn bottles may degrade the adsorptive purity. Accordingly, it may affect the measurement accuracy.

2. Start the **BELSORP-max** measurement software. Close all valves when the software has been already started and valves are open. Press the System button at the lower left on the "Flow circuit diagram" window.

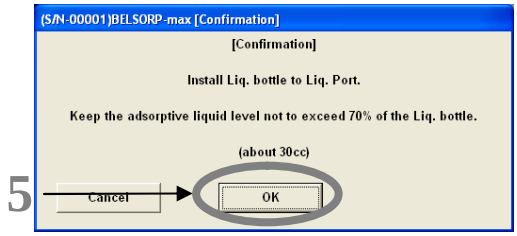


3. A window appears as shown on the right. Select "Degassing the liquid adsorptive".

4. When the "Confirmation" window is displayed, select Yes. In the following step **5.** and later, follow the guidance messages displayed on the "Confirmation" window.

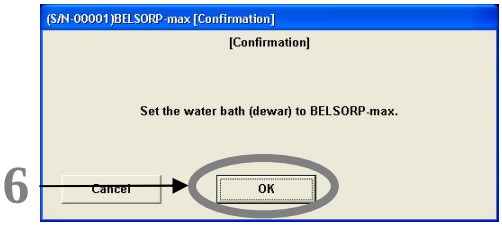


5. Install a liq. bottle according to "How to install sample cells and Liq. Bottles, P.57". When it is complete, press the OK button.



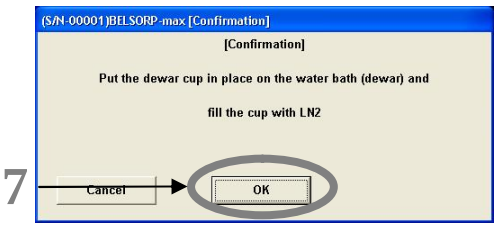
> Keep the adsorptive liquid level lower than 70% of the liq. bottle. When you perform the following degassing process with too much liquid in the bottle, the liq. bottle may be broken.

6. Install the water bath (Dewar vessel) to the instrument.



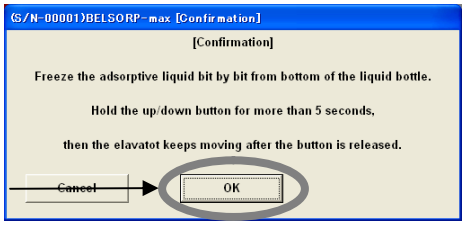
7. Fill fully the Dewar cup with liquid nitrogen. When it is complete, press the OK button.

> Careful attention is required in handling liquid nitrogen.



8. Install the Dewar cup to the top of the water bath (Dewar), and start freezing the adsorptive in the liq. bottle with liquid nitrogen. Press the lifting switch ▲ button on the front of the main unit to lift up the water bath (Dewar). If the button is depressed for more than 5 seconds, the water bath keeps moving up even the switch is released. Press the ■ button to stop it.

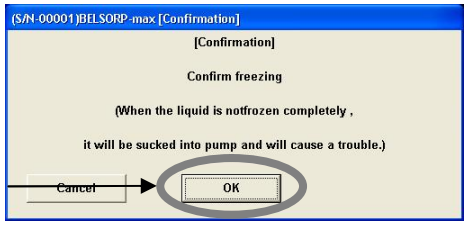
9



9. When the bottom of the liq. bottle comes into contact with the liquid nitrogen, the liquid (adsorptive) in the liq. bottle starts freezing gradually. Lift up the Water bath (Dewar) as the liquid nitrogen level drops, so that the bottom of the liq. bottle keeps contact with the liquid nitrogen. When the adsorptive in the liq. bottle has frozen completely, press the OK button.

10. Verify that the adsorptive in the liq. bottle has frozen completely, and then start vacuuming. Press the OK button. Vacuuming will start automatically (for about 5 minutes).

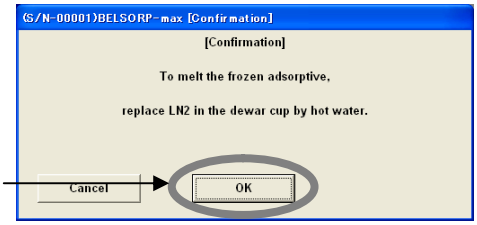
10



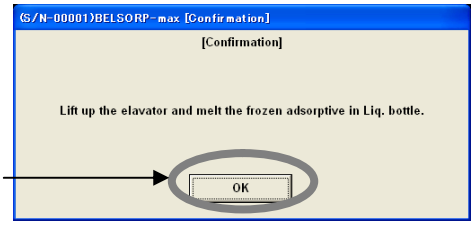
11. When vacuuming is complete, the water bath is lowered to the bottom limit.

12. Remove the liquid nitrogen in the Dewar vessel, and fill it with hot water. Install it to the top of the water bath. Press the OK button. Then a message appears as shown on the right. Lift up the water bath (Dewar) so that the frozen liq. bottle is soaked into hot water to melt the adsorptive in the bottle.

12

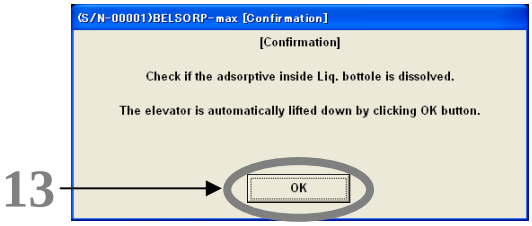


12

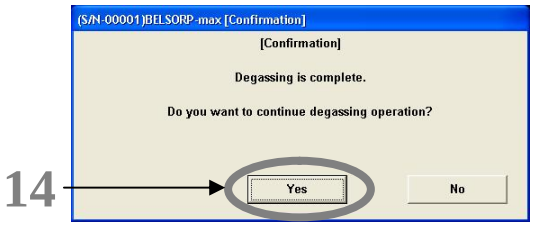


⚠ Careful attention is required in heating the liq. bottle. Heating (melting) partially a frozen liq. bottle may break it.

13. When degassing in step **12.** is complete, the "Confirmation" window appears as shown on the right. Lower the water bath (Dewar) and verify the adsorptive in the liq. bottle has melted completely. It may not have melted completely depending on the type and quantity of the adsorptive in the liq. bottle. If it is not melted completely, lift up the water bath (Dewar) and leave it for a while. It will melt completely. Then, press the OK button.



14. For obtaining accurate measurement data, repeat degassing steps **3.** to **13.** for a total of over 3 times. The degassing process is now complete.

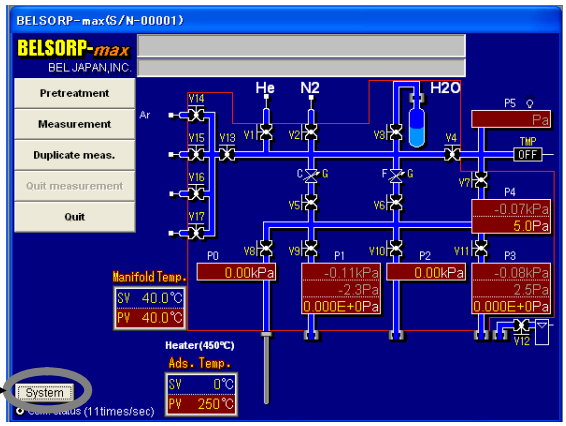


ooo Optional settings ooo

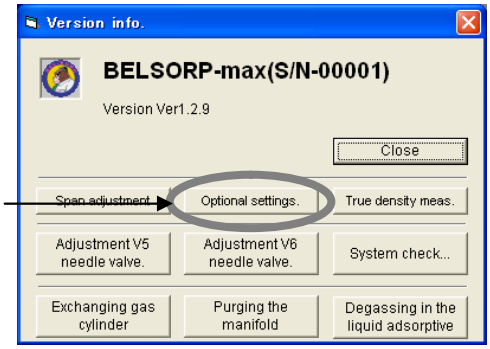
Optional settings can be specified, including the heater, electric furnace, water bath (optional), as well as standard Dewar vessel. Measurement at various adsorption temperature levels is available by using the optional heater, electric furnace, or water bath. Pretreatment (vacuum/flow gas pretreatment) is also available by using the optional heater, electric furnace, or water bath.

1. Start the BELSORP-max main unit and the measurement software.

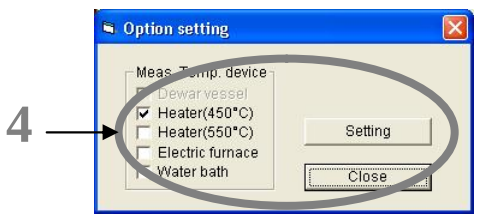
2. Press the System button on the "Flow circuit diagram" window. The "System version information" window appears.



3. Select the Optional settings button. The "Option setting" window appears.



4. Check Heater (450 °C), Heater (550 °C), Electric furnace, or Water bath to be used, and then select the Setting button. Dewar vessel shall always be checked. The heater or electric furnace can be controlled for the adsorption temperature by the software. Select the Close button to return.



ooo Measuring true density ooo

True density is obtained by quantity of solid / powder dividing effective volumetric capacity. In the case of the BEL SORP max, true density is calculated in the following way. At the first, the sample volumetric capacity is calculated by "sample weight after pre-treatment / (blank sample cell 1 −blank sample cell + sample 2)", each of volumetric capacity measured by He. BELSORP-max has a function which automatically covers various tasks from measuring the true density of a solid/powder to outputting data simply after measurement conditions are set and the sample is weighed. Measurement accuracy is 35 ± 0.007 cm^3 (= ± 0.02 %).

* Please measure enough sample weight to increase measurement accuracy.

1. General

1. Set measurement parameters, and start measuring true density.

2. Start blank Vd measurement.

To measure blank Vd:	To skip blank Vd measurement:
1) Install an empty sample cell to port 2. 2) Install the water bath and detachable thermostatic bath, raise water bath, and wait for 70 minutes until the temperature is stabilized. Then, measure blank Vd. ⚠ Set the water bath tempetrature at 40 °C in advance.	Entry values are used. Go to the pretreatment of the sample.

3. Start the pretreatment of the sample.

Start the pretreatment of the sample according to the preset pretreatment parameter. Weigh the sample, and then go to "Sample-available Vd measurement" (If skipping pretreatment, weigh the sample, and then go to "Sample-available Vd measurement".).

4. Start "Sample-available Vd measurement".

1) Install the pre-processed sample cell to port 2.

2) Install the circulating water bath and detachable thermostatic bath, raise water bath, and wait for 70 minutes until the temperature becomes stable. Then, perform "Sample-available Vd measurement".

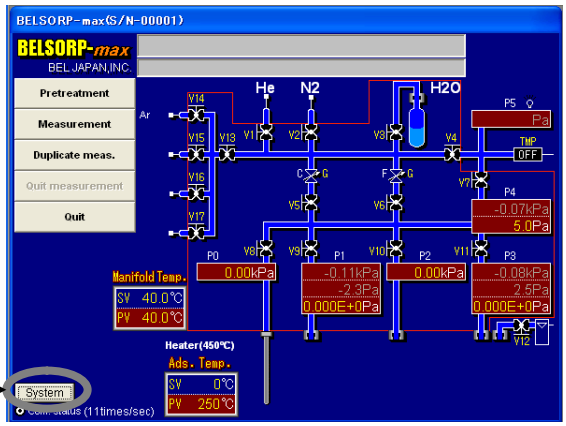
5. The data of true density measurement is saved in the specified file "…DENn.CSV".

2. Procedure of measurement

BELSORP-max's measurement software is equipped with a guidance function to ensure measurement of true density without problems. In this section, a procedure to measure true density in accordance with this guidance is described.

1. Start the BELSORP-max main unit and the measurement software.

2. Press the System button on the "Flow circuit diagram" window. The "System/Version Information" window appears.

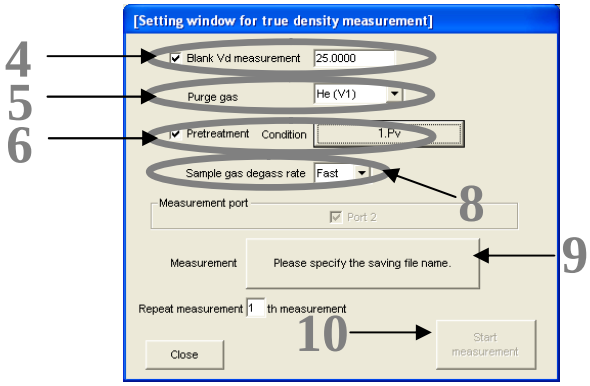


3. Select the true density measurement button. The "true density measurement parameter settings" window appears.

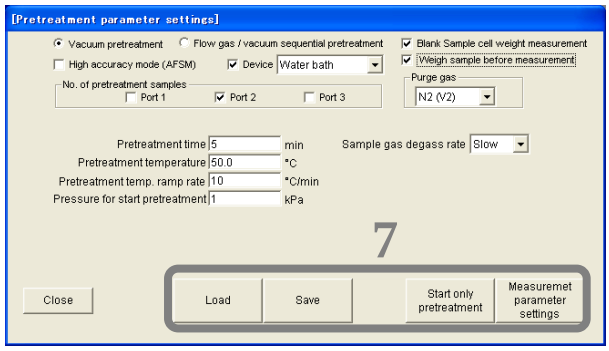
4. Check if performing "Blank Vd measurement". Fill in the measured value of the blank Vd measured in advance otherwise.

5. Select a gas to purge inside of the sample cell after the pretreatment.

6. To perform pretreatment by the main unit, check "Pretreatment" to set up parameters. By selecting the "Pretreatment parameters" button, the window appears as shown on the right. For the setup method of each item, refer to "Pretreatment on P. 111". If not checked, pretreatment is not performed. Pre-treat the sample by the optional pretreatment instrument (BELPREP-flow II/BELPREP-VAC II) as needed.

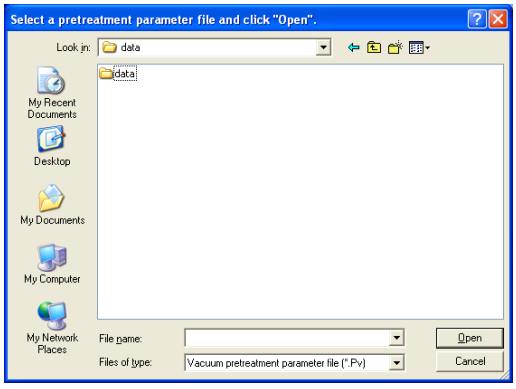


7. Load and save the “Pretreatment parameter setting” file.

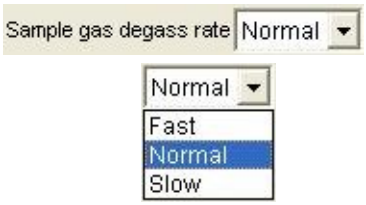


Load	Select the [Load] button to load the existing “Pretreatment parameter setting” file. However, it is necessary that the file has been saved by the [Save] button in advance. After the file has been loaded, select the [Overwrite] button to return to the screen of step 4.
Save	Select the [Save] button to save the existing “Pretreatment parameter setting” file, and return to the screen of step 4.
Overwrite	Select the [Overwrite] button to over write the “Pretreatment parameter settings” file, and return to the screen of step 4.
Delete	Select the [Delete] button to cancel the setting, and return to the screen of step 4. Set the pretreatment parameter again.

When you select the [Load] or [Save], the “Pretreatment parameter file” window appears. Specify the “location to load from” or the “location to save in”. Select or enter the “file name”, and then select the “Open” or “Save”. An extension of “.Pv” is automatically set to the vacuum pretreatment parameter file, whereas “.Pf” is set to the vacuum / flow gas sequential pretreatment parameter file.



8. Select the sample gas degassing rate using [▼] button.

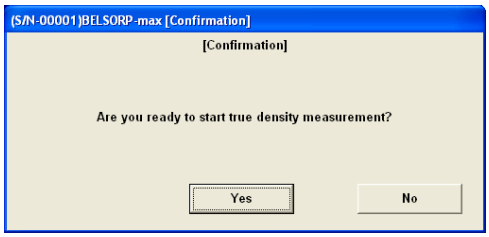


9. Specify a name of the file to save the true density measured data. Set a place to save, enter a file name, and select “Save”. “-Den” is automatically appended to the file name of the measured data, and the extension is “.CSV”.

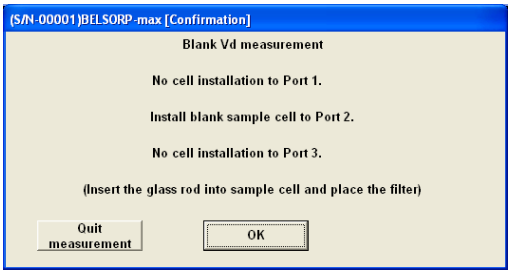
10. Select the [Start measurement] button to start measuring true density. After measurement has started, follow the window displayed.

Now, this section explains the flow when "Blank Vd measurement" and "Pretreatment" are checked.

11. Select the Start measurement button. Then the Confirmation window is displayed. By selecting Yes, true density measurement starts. Or select No to return to the "True density measurement parameter" window.

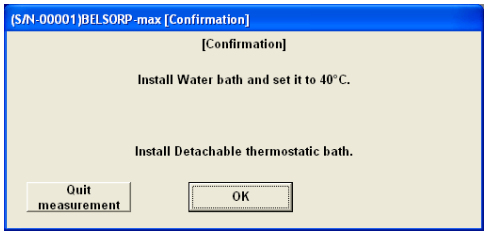


12. The window as shown on the right appears. Install the empty sample cell inserted the glass rod and attached the filter, and select the OK button. By clicking the Quit measurement button, measurement will be aborted, and return to the "True density measurement parameter" window.

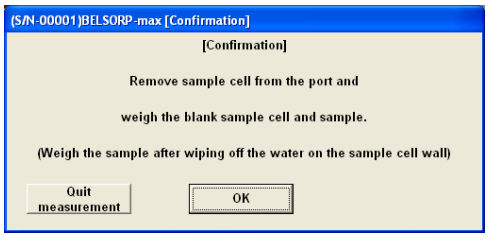


⚠ Only port 2 is used for real density measurement. Insert the glass rod into the sample cell, and attach the filter.

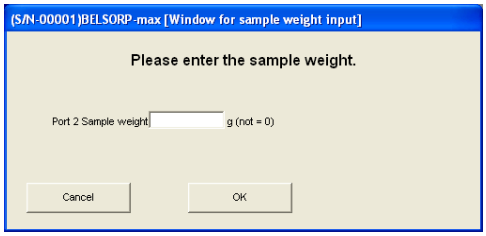
13. Install the water bath and detachable thermostatic bath, and select the the OK button. Raise the water bath, wait for 70 minutes until the temperature is stabilized, and measure blank Vd.



14. When blank Vd measurement has finished, the water bath is lowered, and the confirmation window as shown on the right appears. Weigh the empty sample cell, sample, and select the OK button. Pretreatment is performed continuously based on the pretreatment parameter which was set up at step 6. Follow the direction on the window.



15. After pretreatment, the confirmation window as shown on the right appears. Weigh the sample to enter the measured weight, and select the OK button.



16. Install the sample cell, and select the OK button. In the same manner as applied to step 13, install the water bath, wait for temperature to become stable, and start “Sample-available Vd measurement”.

17. True density measurement has finished when the message as shown on the right appears.

Measurement data

The data below are included in saved files.

Vdb / cm^3	Average value of “blank Vd”
Vds / cm^3	Average value of “sample-available Vd”
Sample weight / g	Mass entered at step **15**
Sample density / g cm^{-3}	True density = measurement result

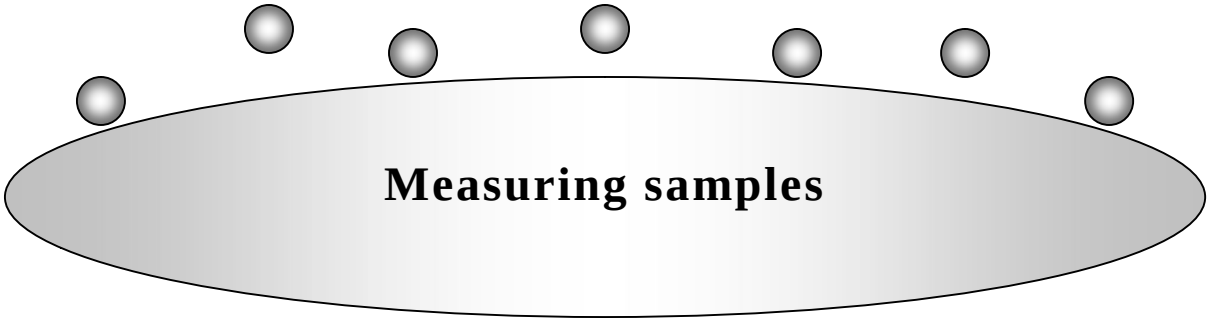
Blank (Vs+Vd)

Pressure	55kPa	60kPa	65kPa	70kPa	75kPa	80kPa	85kPa	90kPa	95kPa	100kPa	105kPa	110kPa
Pen-1	47.48773235	52.17401389	57.47903019	62.21737589	68.09753316	72.61931541	76.95979541	82.67575961	86.81645808	91.57879761	97.25142374	101.5880652
Pe2n-1	47.51298125	52.20247784	57.51183662	62.25657263	68.13766875	72.66048649	77.00519292	82.72450319	86.87111845	91.63316167	97.30688715	101.6486878
Ten-1	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15
Te2n-1	313.15	313.15	313.1691781	313.15	313.15	313.15	313.15	313.15	313.15	313.1705479	313.15	313.15
Pin	54.1169063	59.6847047	64.19357017	70.5352276	74.50459784	78.77555034	85.06354404	88.56623963	93.57895555	99.62817633	103.4152358	108.6791101
Pen	52.17401389	57.47903019	62.21737589	68.09753316	72.61931541	76.95979541	82.67575961	86.81645808	91.57879761	97.25142374	101.5880652	106.5757465
Pe2n	52.20247784	57.51183662	62.25657263	68.13766875	72.66048649	77.00519292	82.72450319	86.87111845	91.63316167	97.30688715	101.6486878	106.6397401
Tin	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15
Ten	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15
Te2n	313.15	313.1691781	313.15	313.15	313.15	313.15	313.15	313.15	313.1705479	313.15	313.15	313.15
Vdb	35.27679222	35.30689097	35.31885333	35.24407926	35.24809881	35.26781583	35.2916542	35.3169899	35.25960807	35.3083075	35.26026947	35.28564422

Sample (Vs+Vd)

Pressure	55kPa	60kPa	65kPa	70kPa	75kPa	80kPa	85kPa	90kPa	95kPa	100kPa	105kPa	110kPa
Pen-1	47.31250197	53.49853531	57.82670008	62.731024	67.18962473	72.90189393	77.33204788	81.94042761	87.61540735	92.00835602	96.50045897	101.5292148
Pe2n-1	47.34136762	53.52646583	57.85935918	62.76634255	67.22863302	72.94478541	77.37969828	81.99019659	87.66824113	92.06327101	96.55921958	101.5889738
Ten-1	313.15	313.16	313.15	313.15	313.15	313.17	313.15	313.15	313.15	313.15	313.15	313.15
Te2n-1	313.1697183	313.15	313.15	313.15	313.1791667	313.15	313.15	313.15	313.15	313.15	313.15	313.15
Pin	56.04532582	59.61786778	64.76181297	69.03822582	75.26028244	79.17982275	83.85958904	89.9791195	93.84606959	98.38622097	103.6285905	108.6235286
Pen	53.49853531	57.82670008	62.731024	67.18962473	72.90189393	77.33204788	81.94042761	87.61540735	92.00835602	96.50045897	101.5292148	106.5302456
Pe2n	53.52646583	57.85935918	62.76634255	67.22863302	72.94478541	77.37969828	81.99019659	87.66824113	92.06327101	96.55921958	101.5889738	106.5924504
Tin	313.1866197	313.15	313.15	313.15	313.1543478	313.15	313.15	313.15	313.15	313.15	313.15	313.15
Ten	313.16	313.15	313.15	313.15	313.17	313.15	313.15	313.15	313.15	313.15	313.15	313.15
Te2n	313.15	313.15	313.15	313.1791667	313.15	313.15	313.15	313.15	313.15	313.15	313.15	313.15
Vds	35.21774427	35.21741023	35.23219405	35.21394756	35.24905503	35.19487274	35.19935896	35.24027135	35.20424569	35.23590031	35.19131936	35.21213978

Vdb	35.28208365	cm3		Sample weight	0.50019	g
Vds	35.21737161	cm3		Sample density	7.730601317	g/cm3



Measuring samples

Measuring with BELSORP-max

ooo For accurate adsorption isotherm ooo

BELSORP-max is a high precision automatic gas-adsorption measuring unit that uses the volumetric method. By the volumetric method, the adsorption to the sample is determined from the adsorptive gas pressure difference using the state equation of gas. Anyone can obtain accurately and quickly, fine particle properties by easy operation, including the specific surface area and the pore size distribution. To obtain data accurately, your careful attention is required for the following points.

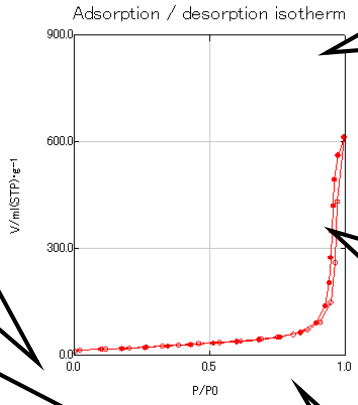
Appropriate amount of samples

The adsorption is determined from the pressure difference due to adsorption. Accurate data cannot be obtained from small amount of adsorption and small pressure difference. Conversely, too much amount of adsorption requires repeated dosing and exhaust, and measurement takes a long time. It is recommended that the **total surface area of the sample be 2 to 40**

No leakage from stop valves or outside

The measurement system keeps negative pressure during adsorption measurement. Accurate data cannot be obtained if there are any leakages at the sample cell connection port from outside. **When you install the sample cell, pay careful attention not to press any foreign materials onto the o-ring.** When the sample scattered in the measurement system adheres to the stop valve, it may result in leakage. **Be sure to use a filter during measurement.**

For accurate adsorption isotherm



Proper sample pretreatment

Correct data cannot be obtained when gas or moisture remains on the sample.

Perform sample pretreatment with the appropriate conditions. Measure the sample mass accurately after pretreatment.

Accurate pressure

The measurement system pressure is measured using a precision pressure sensor and a high resolution A/D converter.

Accurate measurement system volume

The reference volume *Vs* and the dead volume *Vd* are determined with accuracy within 0.1 %.

Appropriate judgment on equilibrium

Accurate isotherm cannot be obtained when the measurement time is too short to reach the adsorption equilibrium. Generally, non-porous samples reach the adsorption equilibrium in 10 minutes at medium or less relative pressure. However, such samples with molecular-sized pores may not reach the adsorption equilibrium even after an extended period. **Judge the equilibrium appropriately for each sample.**

Accurate measurement system temperature

The system reads the temperature at measurement points, and applies temperature correction.

ooo Outline of the measurement ooo

With BELSORP-max, an automatic gas adsorption measurement unit, measurements up to 3 samples can be performed in parallel.

		(AFSM mode)	(Standard mode)
		Measurement of 1 to 2 samples	**Measurement of 1 to 3 samples**
Dead volume change measurement		Yes	No
Measurement port	Port 1	Sample measurement	Sample measurement
	Port 2	Dead volume change measurement	Sample measurement
	Port 3	Sample measurement	Sample measurement
Saturation vapor pressure correction		For saturation vapor pressure, select either "Actual measurement at P0 port" or "Input" mode.	
Dead volume correction		Measurement at Port 2	Refer to the existing DVd file or no dead volume correction

DVd file (data file for dead volume correction)

When you control the measurement temperature using a refrigerant filled in the Dewar vessel, such as liquid nitrogen and liquid argon, the refrigerant level in the Dewar vessel tends to drop due to its evaporation. The dead volume (*Vd*) in the sample cell decreases as the refrigerant level drops; therefore, it is necessary to correct the dead volume change during measurement. When you perform measurement of the dead volume correction using a dead volume reference cell, the data of "ΔVd (ratio of dead volume change) to t (time)" can be saved in the DVd file (data file for dead volume correction). Specify the file name to which the data is saved at "setting the measurement parameter". When you do not perform measurement of the dead volume, the dead volume is corrected by referring to the data file for the dead volume correction that has been measured in advance. Specify the file name from which the data is loaded at "setting the measurement parameter".

ooo Outline of the measurement (low-pressure measurement) ooo

For low-pressure measurements, measurements up to 2 samples can be performed in parallel, using the low-pressure pressure gauge Port 1 (optional) and Port 3.

		(AFSM mode)	(Standard mode)
		Measurement of 1 to 2 samples	**Measurement of 1 to 2 samples**
Dead volume change measurement		Yes	No
Measurement port	Port 1	Sample measurement (optional)	Sample measurement (optional)
	Port 2	Dead volume change measurement	-
	Port 3	Sample measurement	Sample measurement
Saturation vapor pressure correction		For saturation vapor pressure, select either “Actual measurement at P0 port” or “Input” mode.	
Dead volume correction		Measurement at Port 2	Refer to the existing DVd file, or no dead volume correction.

Low-pressure measurement

For adsorption measurement at low pressure, it is necessary to evacuate the sample sufficiently. BELSORP-max performs sufficient evacuation at “Leak check”. A change in the lower pressure section must be detected using a pressure gauge during measurement; therefore, use the low-pressure specification ports (Port 3 and Port 1) for the measurement.

ooo Measurement sequence ooo

The saturation vapor pressure is measured at P0 port.		An input value is used as the saturation vapor pressure.	
With dead volume change measurement	**Without dead volume change measurement**	**With dead volume change measurement**	**Without dead volume change measurement**

1. Sample pretreatment

Perform the pretreatment under such conditions that the gas and moisture adsorbed on the surface can be removed without denaturalizing the sample. Measure the sample mass after pretreatment.

For the pretreatment with BELSORP-max, refer to "Pretreatment, P. 122".

Pretreatment can be performed independently by using optional pretreatment unit, BELPREP-flow II or BELPREP-vac II.

2. Starting the BELSORP-max main unit and the measurement software

Refer to "Starting the BELSORP-max main unit and the measurement software, P. 120".

3. Measurement parameter setting

Refer to "Setting the measurement parameter, P. 128".

4. Starting the automatic sample measurement (system initialization)

Press the Start measurement button on the "Measurement parameter settings" window to start measurement.

5. Preparing the Dewar vessel (or, optional heater, electric furnace, or water bath), and installing the sample cell

Prepare the Dewar vessel and install the sample cell when a window appears showing "【Procedure 1】… to the Dewar vessel (or, the heater, electric furnace or water bath)…, 【Procedure 2】… to Port 1….". Refer to "How to install sample cells …, P. 57". Press the OK button. Then the measurement system is evacuated, and the automatic measurement starts. The gas pressure change and the adsorption isotherm are displayed on the screen during the sample measurement. Refer to "Windows during measurements, P. 159".

6. Leak check

When "Leak check" is selected, the sample cell is evacuated repeatedly while checking the pressure in the sample section until it reaches appropriate condition for measurements.

7. Measurement of the dead volume in the sample cell (room temperature): "when the dead volume measurement before adsorption measurement is selected"

When "non-ideality correction" is selected, the dead volume in the sample cell at room temperature is measured using helium gas. After the measurement, about 100 kPa of helium is dosed to the sample cell.

8. Dead volume measurement at the saturation vapor pressure P0 port (room temperature)

The dead volume in the saturation vapor pressure P0 port (room temperature) is measured using nitrogen. After the measurement, about 100 kPa of nitrogen is dosed to the saturation vapor pressure P0 port.

9. Dead volume measurement in the dead volume reference cell (room temperature) The dead volume in the dead volume reference cell at room temperature is measured using helium gas. After the measurement, about 100 kPa of helium is dosed to the dead volume reference cell. When the adsorptive gas is nitrogen and the adsorptive temperature is 77 K to 78 K, or when the adsorptive gas is argon and the adsorptive temperature is 77 K to 78 K or 87 K to 88 K, the adsorptive gas is used for the measurement.		**9. Dead volume measurement in the dead volume reference cell (room temperature)** The dead volume in the dead volume reference cell at room temperature is measured using helium gas. After the measurement, about 100 kPa of helium is dosed to the dead volume reference cell. When the adsorptive gas is nitrogen and the adsorptive temperature is 77 K to 78K, or when the adsorptive gas is argon and the adsorptive temperature is 77 K to 78 K or 87 K to 88 K, the adsorptive gas is used for the measurement.	

10. Setting up the Dewar vessel (or, optional heater, electric furnace, or water bath)

The Dewar vessel moves up automatically, and the sample cell is soaked into liquid nitrogen or argon.

⚠ Do not place any foreign material on the Dewar vessel.
⚠ Liquid nitrogen may spill out sometimes. Careful attention is required.

11. Measurement of the dead volume in the sample cell (adsorption temperature): "when selecting the dead volume measurement before the adsorption measurement"

The dead volumes in each sample cell at adsorption temperatures are measured using helium gas. Refer to "Dead volume measurement, P. 15". After the measurement, helium in the sample cell is degassed.

12. Condensing adsorptive gas in the saturation vapor pressure P0 port When nitrogen or argon is used, the adsorptive gas may be condensed. Refer to "Saturation vapor pressure measurement, P. 18".	

13. Adsorption measurement

Dosing and adsorption are repeated until the equilibrium pressure reaches the target adsorption pressure. Refer to ”Adsorption measurement and desorption measurement, P. 17”. The data is saved in the relevant file specified for each measurement point. When all the target adsorption pressure values are cleared, it proceeds to the desorption measurement.

14. Desorption measurement

Depressurizing and desorption are repeated until the equilibrium pressure reaches the target desorption pressure. Refer to ”Adsorption measurement and desorption measurement, P. 17”. The data is saved in the relevant file specified for each measurement point. When all the target desorption pressure values are cleared, it proceeds to the next step.

15. Duplicate measurement

When you start “Duplicate measurement, P. 156”, it performs the degassing process (to evacuate the sample for the time specified), and then performs the desorption measurement as many times as specified.

16. After the measurement

When the dead volume measurement “after the adsorption/desorption measurement” is selected, it performs the following measurements.

Dead volume measurement in the sample cell (adsorption temperature)

Dead volume measurement in the sample cell (room temperature): when “non-ideality correction” is selected.

17. Post-treatment

The measurement system is degassed, and then the Dewar vessel moves down. It performs purging and enters the weight according to the settings.

18. Exiting the measurement software and shutdown of BELSORP-max

Refer to “Exiting the measurement software and shutdown of BELSORP-max, P. 166”.

⚠ **When the liquid nitrogen level drops below the sample section or the saturation vapor pressure P0 port, the adsorbed or condensed nitrogen or argon on them may evaporate and generate higher pressure than atmospheric pressure. This may not only cause an error of the measurement data, but also may result in damage to the instrument since it raises pressure in the glass tube, and over time the glass tube is detached from the instrument connection port. This measurement software aborts the sample measurement and degasses the system automatically, when the measurement port pressure exceeds 130 kPa, or the saturation vapor pressure measurement port pressure exceeds 110 kPa. Careful attention is required when you perform measurements for 60 hours or more (For low-pressure measurement, the software manages the time elapsed, and performs the specified post-treatment (post-dead volume measurement, etc.) forcedly, when the measurement lasts 60 hours or more.) .**

ooo Starting the BELSORP-max main unit and the measurement software ooo

1. Starting the BELSORP-max main unit

1. Turn on the power switch on the back of the unit. The power indicator on the front of the main unit lights on.
2. Turn on the rotary pump.
3. When the instrument has not been used for a long time period, refer to “Installing and replacing gas cylinders, P. 90”.

Caution

Turn on the instrument first, and then turn on the pump.

- **When power is supplied to the rotary pump from an external power supply, and the rotary pump is turned on with the instrument turned off, air may be sucked from a vent valve opened. This may result in overheat or failure of the pump.**

2. Starting the measurement software

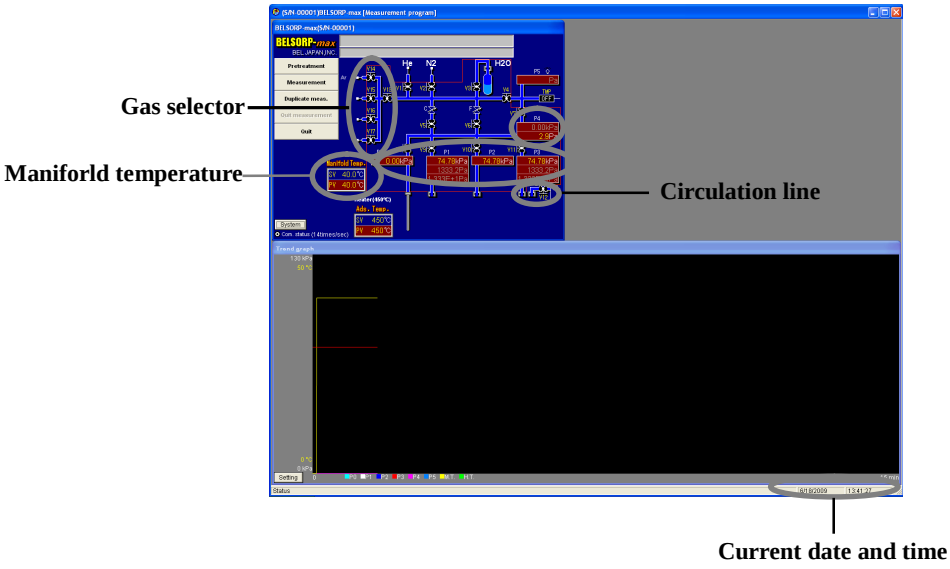
1. Verify that the main unit and the personal computer are connected properly using a connection cable.
2. Check that power is supplied to the instrument.
3. Turn on the personal computer, and start “Windows”.
4. Select “Start” > “Program” menu > “BELmax” > “BELmax”.

5. The measurement software starts, and the “Main” window appears. When the current status is displayed for the following items, startup is complete (The screens shown below are those in the Windows XP mode.).

・Current date and time

・Pressure gauge (P0 to P4)

・Manifold temperature (TIC1)



The following items are displayed when you select them as options.

・Gas selector (V13 to V17)

・Flow gas pretreatment line (V12)

6. In the event of error in the communication line, including such cases that the main unit and the personal computer are not connected properly using a connection cable, the “Communication error” window is displayed. Check the power supply to the main unit and the connection.

* If the valves (V1 to V10) still remain as opened manually when the software was used previously, all valves close when the software starts.

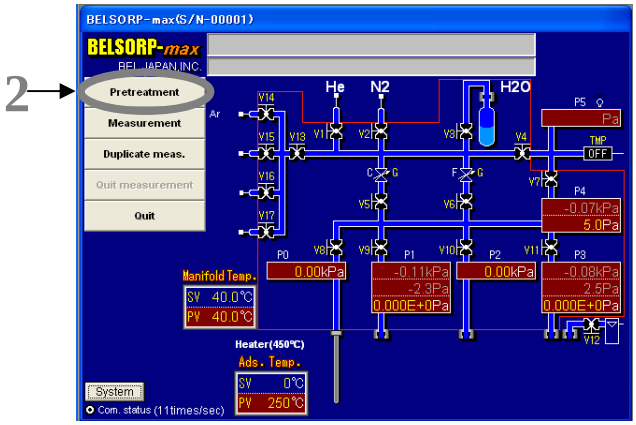
ooo Pretreatment ooo

Before you start measurements with BELSORP-max, perform weighing and pretreatment of the sample to be measured. [When you perform pretreatment of the sample with this instrument (the software requests you to select "weighing samples before the measurement" or "weighing samples after the measurement"), a message related to weighing samples appears. Follow the instructions in the message. When you perform pretreatment of the sample with an optional pretreatment device (BELPREP-flow II, BELPREP-VAC II), weigh samples independently.]

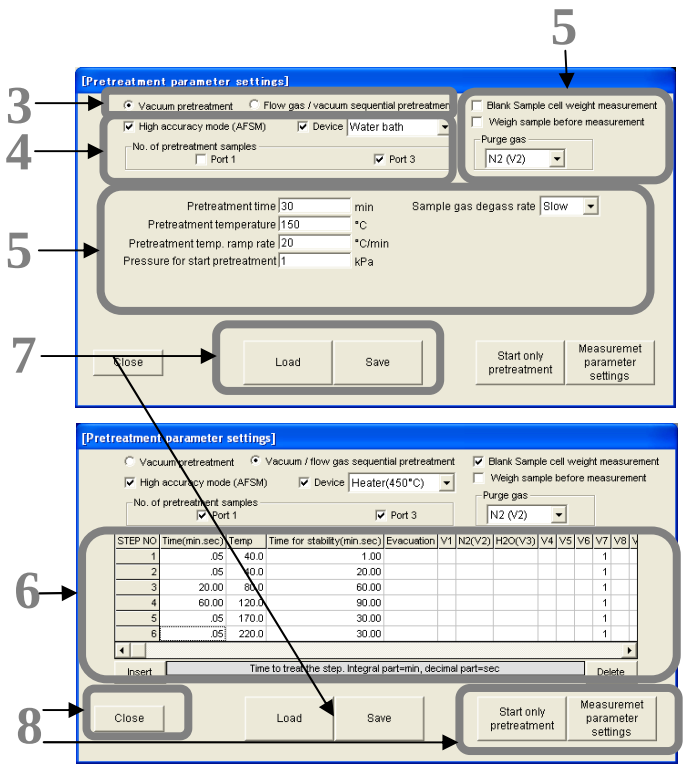
This manual describes the sample pretreatment with this instrument (at pretreatment temperature using the heater, electric furnace, or water bath).

1. Start the BELSORP-max main unit and the measurement software.

2. Select the Pretreatment button on the "Flow circuit diagram" window.



3. The Pretreatment parameter settings window appears. Select either Vacuum pretreatment or Vacuum/flow gas sequential pretreatment. The flow gas sequential pretreatment can be performed only when the flow gas pretreatment line is provided.

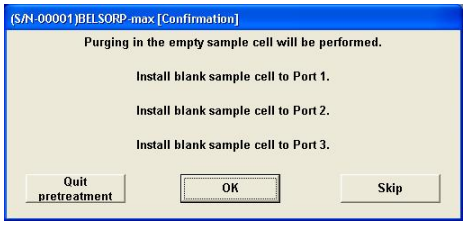


4. Specify the AFSM, device, and pretreatment samples.

AFSM	When you measure with a dead volume reference cell, check AFSM (Port 2 is used for the reference cell.).
Device	When you use an adsorption temperature device, check Device and select the device using ▼ button. Setting for the device shall be in accordance with "Optional settings, P. 107".
Pretreatment samples Port 1 to 3	For the sample cell to be used, check Port 1, Port 2, or Port 3. The port used for the dead volume change measurement is not displayed, and cannot be selected. Check at least one of them.

5. When the vacuum pretreatment is selected, specify the following items.

Pretreatment time	Enter the pretreatment time in minutes (contein none of rump time).
Pretreatment temperature	Enter the pretreatment temperature in °C. Specify the temperature from the personal computer when the device is the heater or electric furnace.
Pretretment temp. ramp. rate	Enter the pretreatment temp. ramp. rate in °C /min^{-1} . 450 ^{o}C / 550 ^{o}C heater: Setting pretreatment temp. ramp. rate 1-20 ^{o}C min^{-1} Electric furnance (- 1000 ^{o}C) : Setting pretreatment temp. ramp. rate 1-100 ^{o}C After heating enable to pressure attainment, first heated to "(Pretretment temperature) – (Pretretment temp.ramp. rate)", and then heated to "Pretretment temperature"
Heating enable to pressure	Enter the pressure to start heating in kPa. When the pressure drops below the specified level, the device moves up and it starts heating. Setting for the device shall be in accordance with "Optional settings, P. 107". ⚠ Please note that if there is a possibility of rapid heating to sccatter.
Sample gas degassing rate	Select the appropriate sample gas degassing rate using ▼ button. Select "Slow" to degas slowly to prevent the sample from scattering. Select "Normal" to degas stepwise to prevent the sample from scattering. Select "Fast" to degas quickly.
Weighing samples before the measurement	Check "Weigh sample before measurement" to weigh the sample after pretreatment. When checked, a window appears to prompt you to weigh after the pretreatment.

Blank sample cell weight measurement	Check this when you measure the blank sample cell weight. When you check it, a window appears to prompt you to install a blank sample cell. Once installed, it evacuates the sample cell in the gas purging process. At the evacuation, a window appears as shown on the right. When you mistakenly install the sample cell with a sample in it, select Quit pretreatment or Skip. Press OK to start evacuating the blank sample cell. 
Purging after the measurement	Check this to purge after the measurement. Select the purge gas using ▼ button. It purges when weighing the blank cell and the sample. ⚠ Warning: Do not purge with dangerous gas.

6. When selecting the flow gas / vacuum pretreatment, specify the following items.

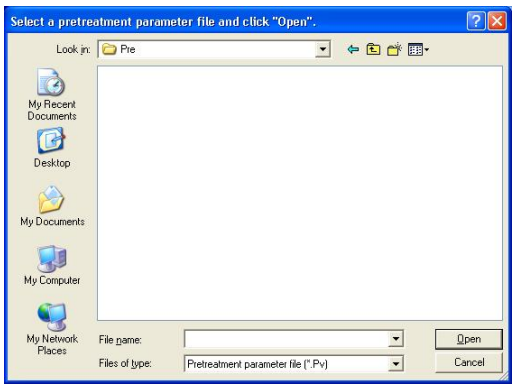
Time (min., sec.)	Specify the treatment time required for this step. The integer part represents the time in minutes and the decimal part represents the time in seconds. The sum of the minutes and seconds is the treatment time in this step.
Target temperature	Specify the temperature to complete this step (when you use the heater or electric furnace that can be controlled from the personal computer). When it does not reach the target temperature in the time specified, it waits until it reaches the target temperature ±2 °C.
Time for stability (min., sec.)	Specify the waiting time for stability after the treatment time (min., sec.) is over. The integer part represents the time in minutes and the decimal part represents the time in seconds. The sum of the minutes and seconds is the time for stability.
Evacuation	Specify the evacuation. Set to “0” not to evacuate, “1” to evacuate quickly, and “2” to evacuate slowly.
V1 to 17	Specify the valve open/closed. Set to “0” to close, and “1” to open. Only a single valve can be opened, out of V1 to V3, and V14 to V17. Otherwise, gases are mixed. After closed, the gas accumulator is exhausted for 30 seconds.
Device	Specify the temperature device switch. Set to “1” to turn on the switch, which enables to set the target temperature. Set to “2” to turn off the switch.
FAN	Specify the fan when the electric furnace is selected as the temperature device. Set to “1” to turn on the fan, which cools down the electric furnace rapidly. Set to “0” to turn off the fan.
UP	Specify to move up the elevator. Set to “1” to move it up. Set to “0” not to move it.
DN	Specify to move down the elevator. Set to “1” to move it down. Set to “0” not to move it.

WRG	Specify the indication of the vacuum gauge P5. Set to “1” to indicate. Set to “0” not to indicate.
TMP	Specify the turbo molecular pump. Set to “1” to start rotating. Set to “0” to stop rotating.
Insert button	This is used to insert a line to the line where a cursor is placed. The texts on the line where a cursor is placed are copied onto the line inserted. All the lines below the line where a cursor is placed are shifted a line down.
Delete button	This is used to delete a line where a cursor is placed. All the lines below the line deleted are shifted a line up.

7. Load and save the “pretreatment parameter settings” file, where applicable.

Load	Select the Load button to load the existing “pretreatment parameter setting” file. The file must have been saved using the Save button.
Save	Select the Save button to save the pretreatment parameter settings to the relevant file.

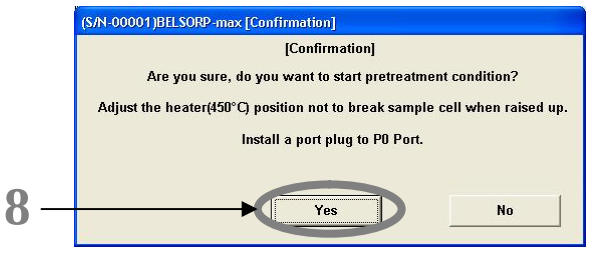
When selecting Load or Save, the “Pretreatment parameter file” window appears. Specify the “location to load from” or the “location to save in”. Select or enter the “File name”, and then select “Open” or “Save”. An extension of “.Pv” is automatically set to the vacuum pretreatment parameter file, whereas “.Pf” is set to the vacuum / flow gas sequential pretreatment parameter setting file. For the rules to enter a file name, refer to the Windows instruction manual.



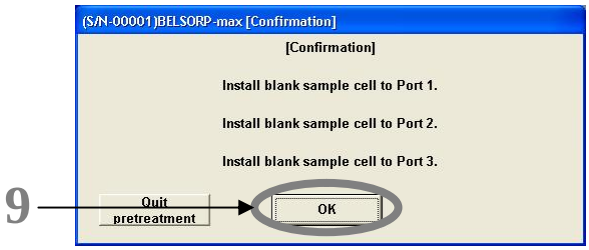
8. Select the Close button to cancel the settings and finishi the pretreatment parameter setting.

Select the Measurement parameter settings button. Then the “Measurement parameter settings” window appears. Parameter setting can be performed in sequence from the pretreatment to the measurement (refer to “Setting the measurement parameter, P. 128) .

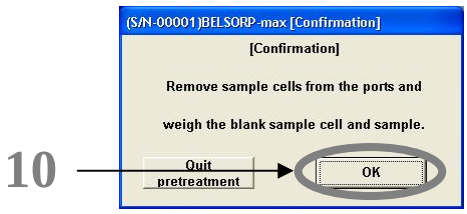
Select the Start only pretreatment button. Then the “Confirmation” window as shown on the right appears. Verify that the sample cell has been removed, and then select the Yes button to start the pretreatment. Select the No button to return to the “Pretreatment parameter setting” window. Once the pretreatment starts, follow the instructions on the window.



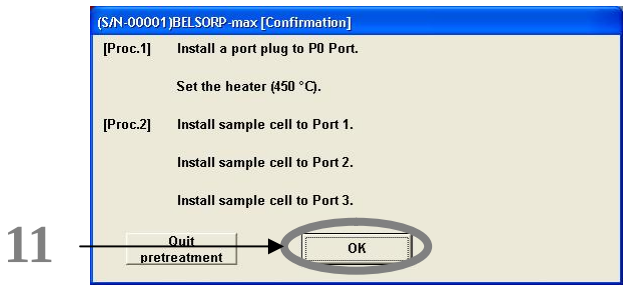
9. Install a blank sample cell to the relevant port, and press the OK button. Then, it evacuates and purges (This is when selecting “weigh samples before the measurement” or “weigh samples after the measurement”. Proceed to step 11, when not selected.).



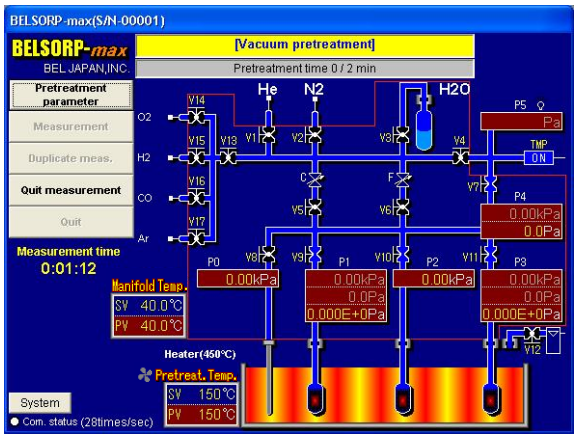
10. Remove the sample cell from the relevant port, weigh the blank cell and the sample, and then press the OK button.



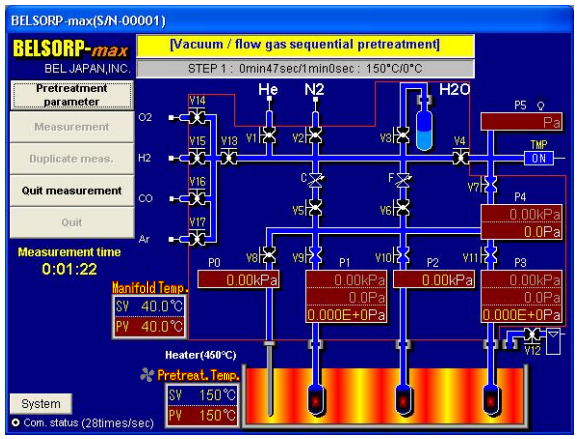
11. When using a device, install the relevant device. Specify the pretreatment temperature for the device that cannot be controlled from the personal computer. Install the sample cell that has been weighed to the relevant port, and press the OK button.



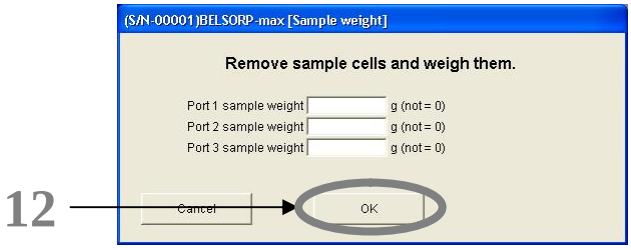
Vacuum pretreatment



Vacuum / flow gas sequential pretreatment



12. When “Weigh samples before the measurement”is checked, the system purges after the pretreatment, and then displays the “Sample weight” window. Weigh the sample, enter the measured weight, and press the OK button.



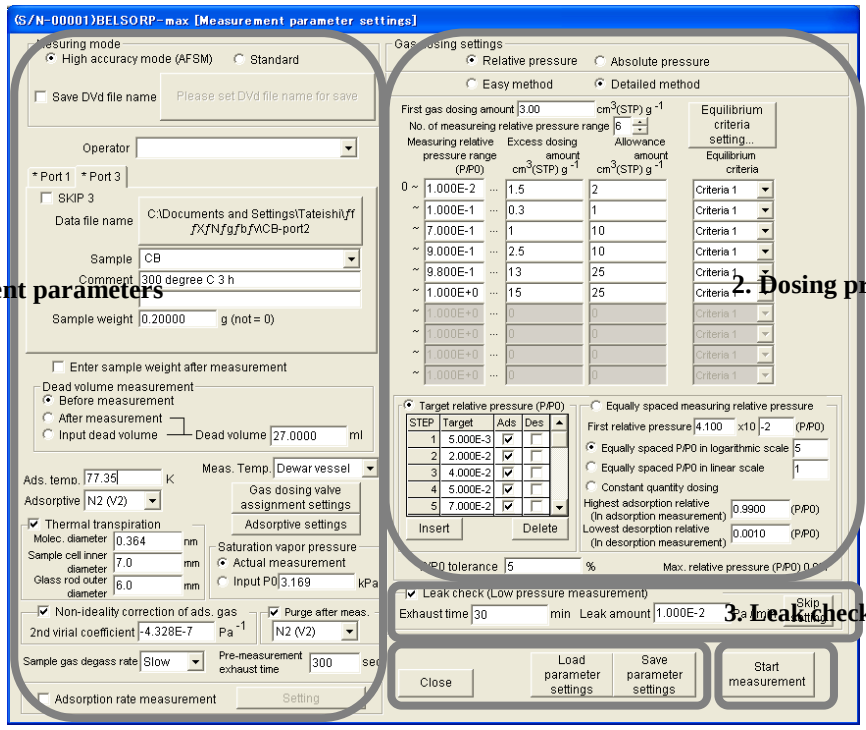
13. When Only start pretreatment button is selected in step **8.**, it finishis the sequence. When Measurement parameter settings button is selected, it proceeds to the measurement. Follow the instructions on the screen.

ooo Setting the measurement parameter ooo

1. Start the measurement software, and select the Measurement button on the "Main" window. It is not necessary to select the Measurement button, when you navigate from "Pretreatment, P. 122" or "Duplicate measurement, P. 156".

2. The "Measurement parameter settings" window appears as follows. Specify the conditions related to the adsorption measurement for the sample.

⚠ Remove the sample cell from the measurement port.

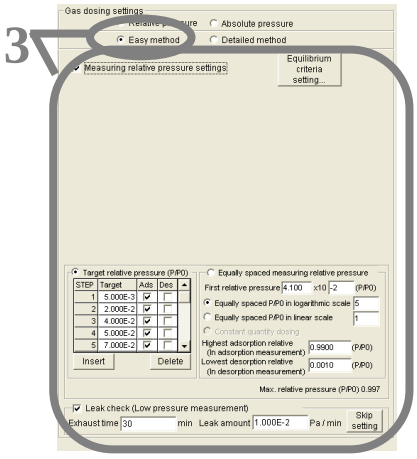


1. Measurement parameters **2. Dosing pressure settings**

3. Leak check parameter setting

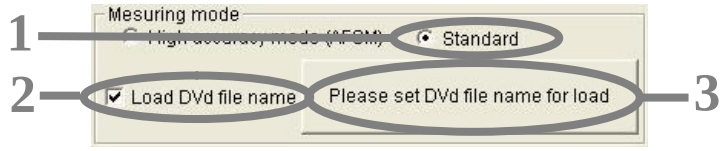
4. Load / Save **5. Start measurement**

3. When you select "Easy method" in "2 . Dosing pressure setting", the screen changes as shown on the right.



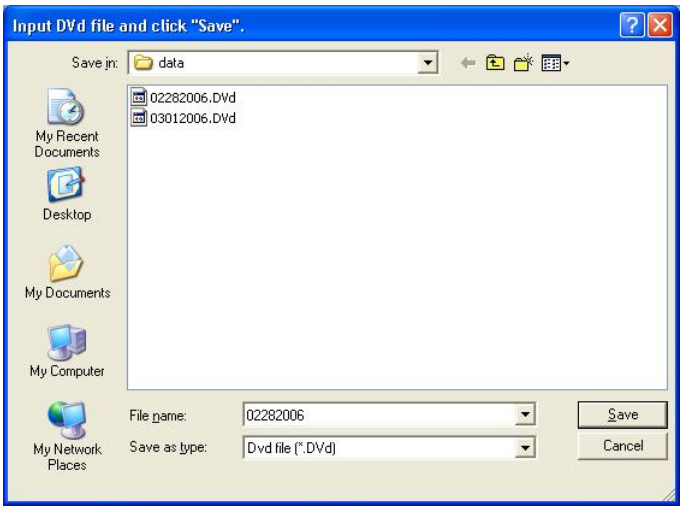
1. Measurement parameters

1. Select the measuring mode.

High accuracy (AFSM)	 Select this mode when you measure the dead volume using a dead volume reference cell. The dead volume changes as the liquid nitrogen level changes. The dead volume data that was measured using a dead volume reference cell can be saved in the relevant file (This mode is effective for the low-pressure measurement using liquid nitrogen; however, it is not necessary for the measurements using the water bath or heater.). These files offer the dead value reference data to the subsequent sample measurement. To save the measured Save DVd file name dead volume data, check and specify the "DVd file name for save".
Standard	 Select this mode when you do not measure the dead volume using a dead volume reference cell. The dead volume changes over time during sample measurement. Therefore, dead volume reference data is required when you do not measure the dead volume using a dead volume reference cell. To refer to the file for the measured dead volume data, check Load DVd file name and specify the dead volume reference data for the "DVd file name for load". At this time, select the dead volume data that was measured using a dead volume reference cell with the same conditions as those for the sample cell to be measured.

2. When [DVd file] is checked, select [Load] to refer to the file for the dead volume data, or select [Save] to save the dead volume data measured using a dead volume reference cell to the relevant file. Once [DVd file] is unchecked, [Load] or [Save] from/to the file is disabled.

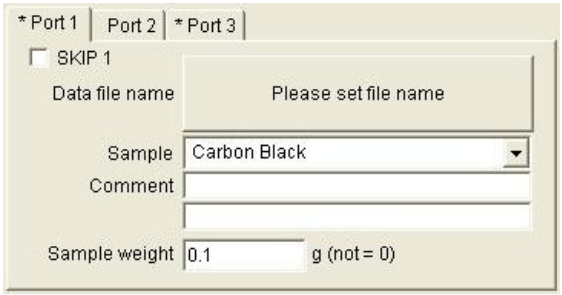
3. Select the Please set DVd file name for save button. Then the "Save DVd file" window appears.



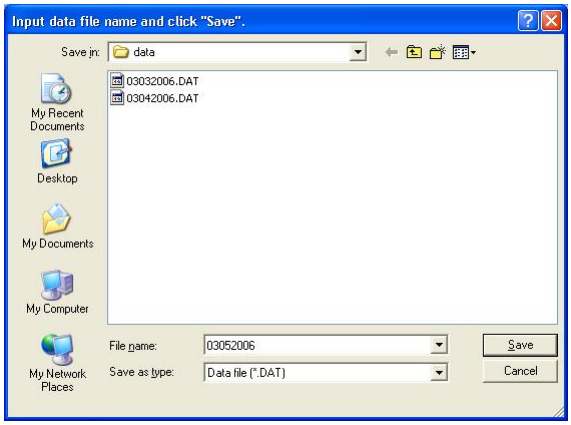
4. Specify the "location to load from" or the "location to save in". Select or enter the "File name", and then select "Save". An extension of ".DVd" is automatically set to the DVd file.
For the rules to enter a file name, refer to the Windows instruction manual.

5. Specify the operator name. 20 operator names can be registered at the maximum.

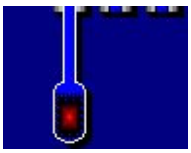
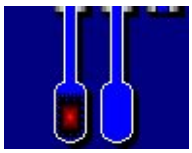
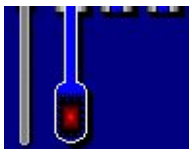
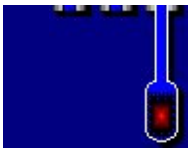
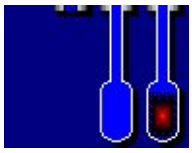
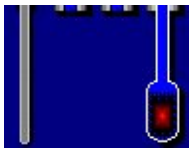
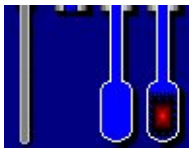
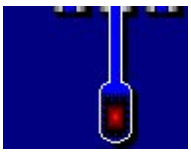
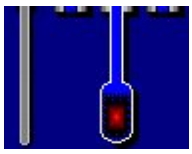
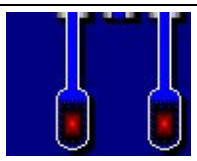
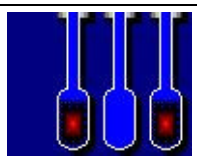
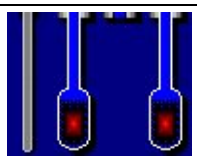
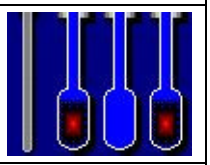
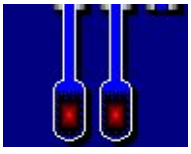
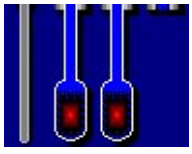
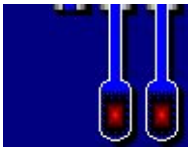
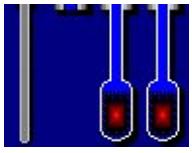
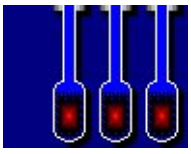
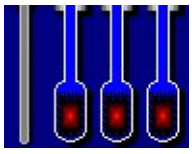
6. Specify the relevant items for each measurement port (Port 1 to Port 3). Port 2 is used (to measure the dead volume) when the AFSM measuring mode is selected; therefore, Port 2 is not displayed.
When "Leak check (low pressure measurement)" is checked, Port 2 is not used for the low-pressure measurement and it is not available for setting.

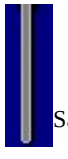


7. Specify the relevant items for the sample to be measured.

SKIP	Uncheck this when the relevant port is used for the measurement. When checked, the relevant port is not available. Items of “Data file name” or below are not displayed. The “ * ” mark is attached to the head of the port number to be used.
Measurement data file name	Select the [Please set file name] button.  The “Save file” window appears. Specify the [location to save in], enter the [file name], and select the [Save] button. An extension of “.DAT” is automatically set to the file. For the rules to enter a file name, refer to the Windows instruction manual.
Sample name	Enter the sample name. Press the [▼] button to display the sample name list entered previously, and select the sample name from them.
Operator name	Enter the operator name. Press the [▼] button to display the operator name list entered previously, and select the operator name from them.
Comment	Enter textual information related to the sample. 200 half-sized characters are accepted at the maximum.
Sample weight (g)	Enter the sample weight measured. When “Weigh sample after measurement” is cheeked, enter an approximate value.

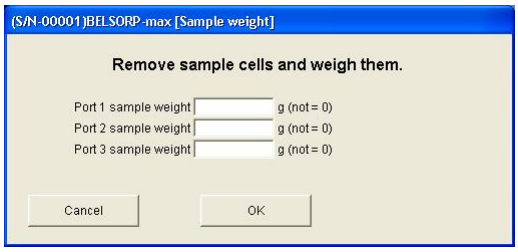
8. Each port is used as combined as follows.

Number of samples to be measured	Low pressure measurement	Port P0 1 2 3	Port P0 1 2 3	Port P0 1 2 3	Port P0 1 2 3
				Saturation vapor pressure measurement using P0 port	Saturation vapor pressure measurement using P0 port
			Dead volume measurement using Port 2		Dead volume measurement using Port 2
1 sample	○				
	○				
	×				
2 samples	○				
	×				
	×				
3 samples	×				

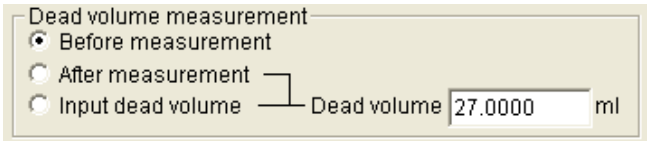
 Sample cell  Dead volume cell  Saturation vapor pressure P0 port

9. Check “Enter sample weight after measurement” where 

applicable.

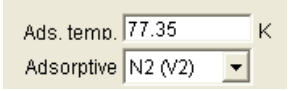
Enter sample weight after measurement	When checked, the “Enter sample weight after measurement” window appears after post-treatment purging after measurement. Enter the sample weight to the relevant port, and select the OK button. The system performs purging without exception; therefore, specify the purge gas used for post-treatment purging. 

10. Select “Before measurement”, “After measurement” or “Input dead volume” for the Dead volume measurement. When “After measurement” or “Input dead volume” is selected, enter the dead volume. During measurement, the adsorption is determined using the input dead volume.



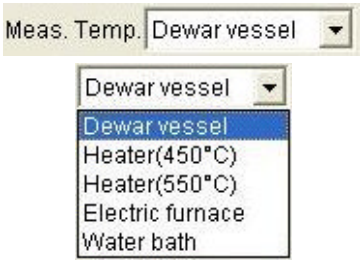
Before measurement	Select “Before measurement” to measure the sample dead volume before adsorption measurement.
After measurement	Select “After measurement” to measure the sample dead volume after adsorption measurement using the “dead volume” entered to the right of the above screen. Then, the adsorption is re-calculated. The nitrogen holding time in a fully filled Dewar vessel is 60 hours; therefore, the system automatically stops the measurement and measures the dead volume when the measurement time exceeds 60 hours, when you select “After measurement”.
Input dead volume	When “Input dead volume” is selected, the sample dead volume is not measured. Enter the dead volume.

11. Specify the adsorption conditions.

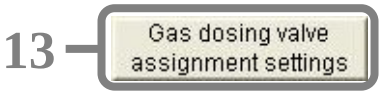


Adsorption temperature (K)	Enter the adsorption temperature in K (Kelvin). The heater or the electric furnace is controlled from the personal computer for the adsorption temperature. Dewar vessel: Enter liquid nitrogen “77.0” to “78.0”. Enter liquid argon “77.0” to “78.0”, or “87.0” to “88.0”. Heater (450 °C): Enter “323.15” to “723.15” (when using an optional device). Heater (550 °C): Enter “323.15” to “823.15” (when using an optional device). Electric furnace: Enter “323.15” to “1373.15” (when using an optional device). Circulation water bath: Enter “278.15” to “343.15” (when using an optional device).
Adsorptive name	Select N_2, Ar, etc. (specified in “Gas dosing valve assignment settings”) using the ▼ button.

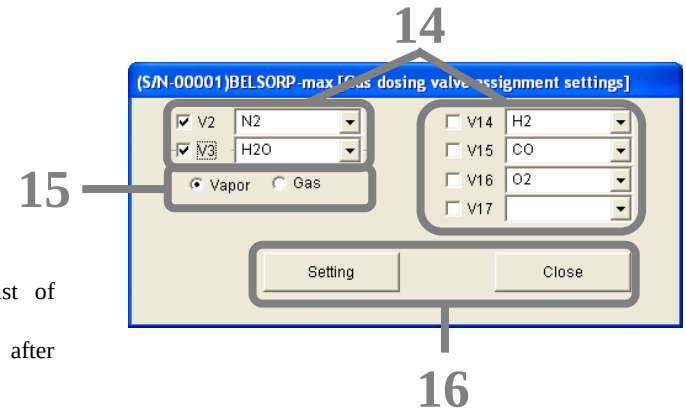
12. The measurement device can be selected from the devices checked in “Optional settings, P. 107”. When only “Dewar vessel” is checked in the optional setting, no measurement device is displayed. Select the appropriate device using the ▼ button.



13. To change the adsorptive name assigned to valve V2, V3, or V14 to V17, select the Gas dosing valve assignment settings button. The following “Gas dosing valve assignment settings” screen appears.



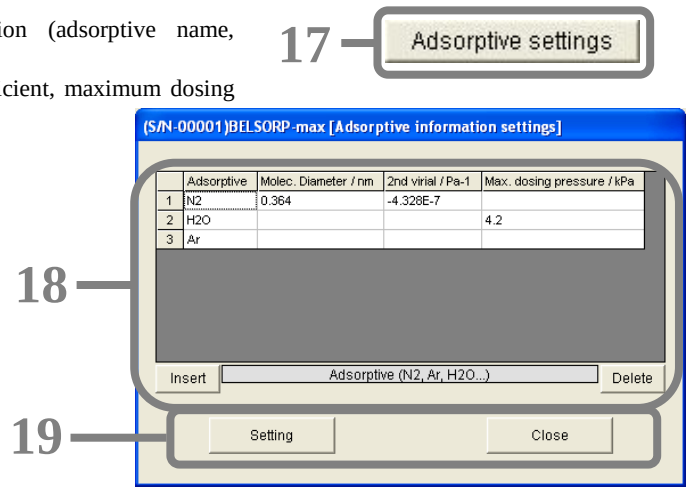
14. Enter directly the adsorptive name, or select it using the ▼ button (specified in “Adsorptive settings”). When checked, it can be selected from the list of “adsorptive name”, and “purge after measurement”.



15. Select Vapor when you connect Vapor to V3 and use it as adsorptive, otherwise select Gas.

16. Select the Setting button. Or, select the Close button to close the window without any setting. Return to the Measurement parameter settings window for additional setting.

17. To change the adsorptive information (adsorptive name, molecular diameter, second virial coefficient, maximum dosing pressure), select the Adsorptive settings button. The following "Adsorptive information settings" window appears. This information of the "molecular diameter", "second virial coefficient", and "maximum dosing pressure" is used as the measurement parameter when the "adsorptive name" is selected in step **11**.



In order to save the information of the adsorbate changed during measurement in JKN, select save in the measurement setting screen after finishing measurement.

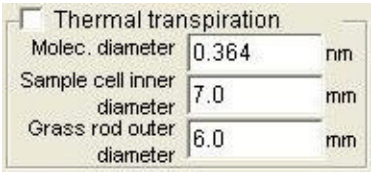
18. Specify the following items.

Adsorptive name	Enter the adsorptive name.
Molecular diameter (nm)	Average molecular diameter is used for the thermal transpiration correction. For nitrogen adsorption, enter "0.364".
Second virial coefficient (Pa^{-1})	For the "adsorptive gas non-ideality correction", enter the second virial coefficient at adsorption temperature when applicable. When not used, it may remain blank.
Maximum dosing pressure (kPa)	For the vapor adsorptive, the system temperature is 40 °C. Therefore, it cannot be dosed at pressure above the saturation vapor pressure at 40 °C. It is recommended to enter the saturation vapor pressure at 30 °C (4.2 kPa in the case of water) in consideration of non-uniform temperature in the manifold temperature. The vapor adsorption measurement cannot be performed since the "Start measurement" button does not change from gray to black without this numerical entry.
Insert button	This is used to insert a line to the line where a cursor is placed. Texts on the line where a cursor is placed are copied onto the line inserted. All the lines below the line where a cursor is placed are shifted a line down.
Delete button	This is used to delete a line where a cursor is placed. All the lines below the line deleted are shifted a line up.

For the molecular diameter and the second virial coefficient, refer to " P.178".

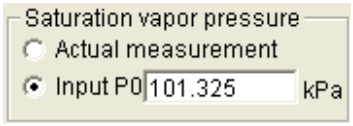
19. Select the [Setting] button. Or, select the [Close] button to close the window without any setting. Return to the [Measurement parameter settings] window for additional setting.

20. For the thermal transpiration correction, check the box and specify the following items.



Molecular diameter (nm)	Enter the average molecular diameter. For nitrogen molecule, enter “0.364”.
Sample cell inner diameter (mm)	The standard sample cell inner diameter is 7 mm. Change the setting when using the sample cell with different inner diameter.
Glass rod outer diameter (mm)	The standard glass rod outer diameter is 6 mm. Change the setting when using a glass rod with different outer diameter.

21. Select either the “Actual measurement” or “Input” mode for the saturation vapor pressure.



Actual measurement	When “Actual measurement” is selected, the value measured at the saturation vapor pressure P0 port is used as the saturation vapor pressure.
Input (kPa)	When “Input” is selected, change the “Saturation vapor pressure” where applicable.

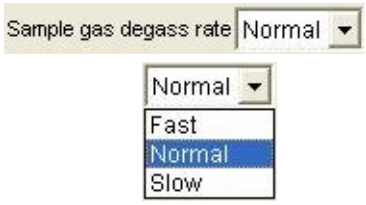
The setting range is limited as follows. ○: Available, ×: Not available

Setting range	Measurement device, adsorptive name, adsorption temperature			
	Dewar vessel			Heater, electric furnace, circulation water bath Except for the adsorptive name and adsorption temperature listed on the left
	N_2: 77K to 78K	Ar 77K to 78K	Ar 87K to 88K	
Actual measurement	○	×	○	×
Input	○	○	○	○

22. When you perform the adsorptive gas non-ideality correction, check the box and specify the second virial coefficient.

Second virial coefficient at the adsorption temperature	When you perform the adsorptive gas non-ideality correction, specify the second virial coefficient at adsorption temperature where applicable.

23. Select the sample gas degassing rate using ▼ button.



Slow	It degasses slowly to prevent the sample from scattering.
Normal	It degasses stepwise to prevent the sample from scattering.
Fast	It degasses quickly.

Generally, select “Normal”. When the sample scatters by selecting “Normal”, select “Slow”. Select “Fast” only when you measure the palletized or granular-shaped sample that does not scatter.

24. This is the exhaust time immediately before the first adsorption measurement point is measured. It is defaulted to 300 seconds. Set the exhaust time where applicable.

25. When you perform the purge after measurement, check this box.

Select the purge gas using ▼ button. When “Enter sample weight after measurement” is checked in step **9.**, the system performs purging without exception. Specify the purge gas.

⚠ Do not use dangerous gas for purging.

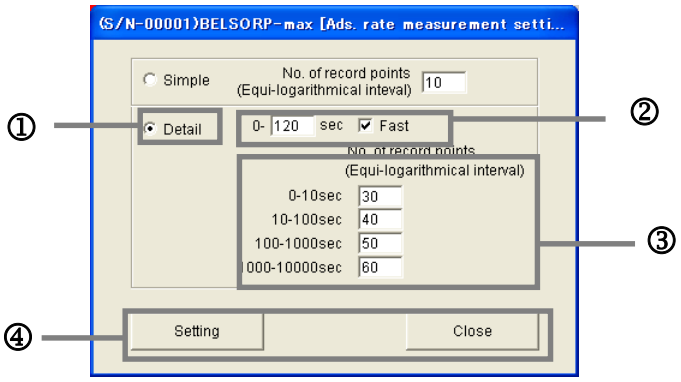
26. To conduct adsorption rate measurement[*1], check 

. (*1 adsorption rate measurement is an optional function.) The adsorption rate measurement is a single sample measurement in Port 3.

In the adsorption rate measurement, pressure change at each measurement point of adsorption side is saved. Further, since pressure change before equilibrium is reached is read with the pressure gauge at the Vs, it is saved as one adsorption point once gas is introduced even when target relative pressure is not reached.

Therefore, the number of measurement points may increase than usual due to inappropriate amount of excessive introduction. In the case of unknown samples, it is recommended to conduct adosorption rate measurement after doing a generally adsorption measurement to determine the appropriate amount of excessive introduction from the adsorption isotherm.

When Setting is selected, following window is displayed.



Select “Simple” in order to save data (pressure value) at certain equi-logarithmical intervals from start of measurement to equilibrium. The minimum data saving interval is the one point per second. Enter number of record points of adsorption time at equi-logarithmical intervals in the column of “No. of record points”. Larger input values result in increase of number of measurement points at each equi-logarithmical interval.

Select “Details” in order to specify data saving intervals each time. In the range of 0~120 seconds, selection of “Fast” enables data saving of about 5~8 points[*2] per second. (*2 Saving intervals depend upon communication intervals.)

[Method of setting “Details”]

①Select “Details”.

②Select “Fast” and enter the storage time (0-120 seconds can be entered).

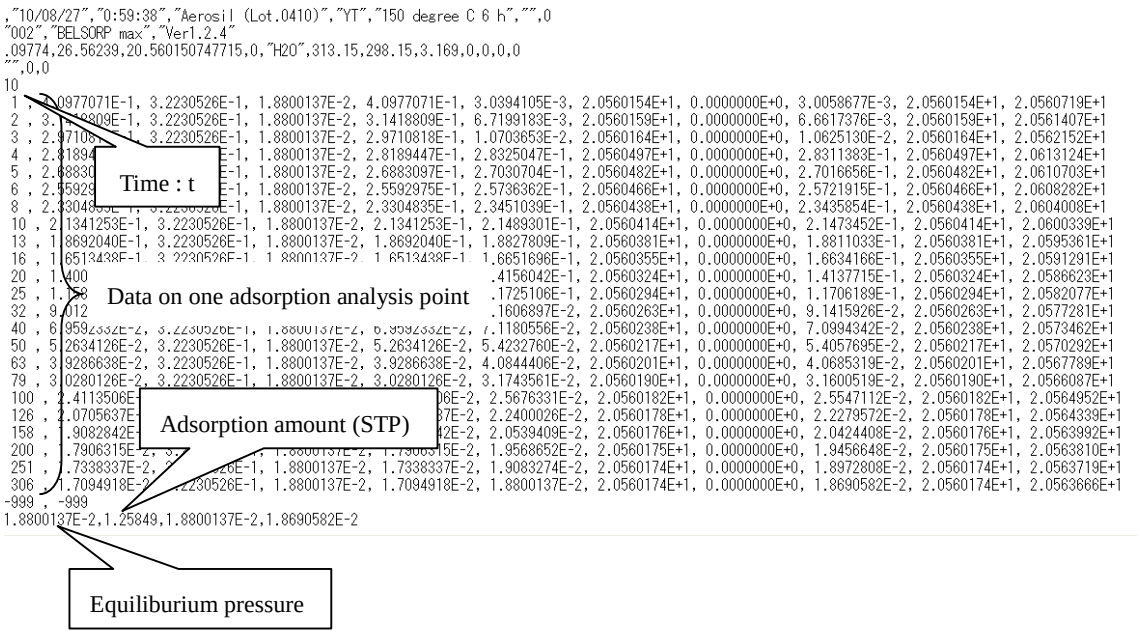
“Fast” is prioritized within the time for which “Fast” is selected. In the case of above setting, input values of “0-10sec” and “10-100 sec” are neglected up to 120 seconds.

When “Fast” is not selected, number of records at equi-logarithmical intervals input for each time is saved.

③Enter number of records at equi-logarithmical intervals in “10-100sec”, “100-1000sec” and “1000-10000sec”. For each time “0-500” points can be entered, and total number of saving is 2000 points.

④Select Setting after setting conditions. Select Close to return to the window for measurement condition setting.

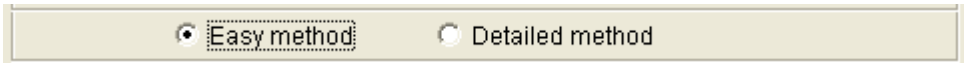
⑤Rate measurement data are saved in “….RAT” data. Conduct analysis using the rate measurement analysis software BEL-Dyna®, or analyze RAT file (CSV type file) graphically using the spreadsheet software.



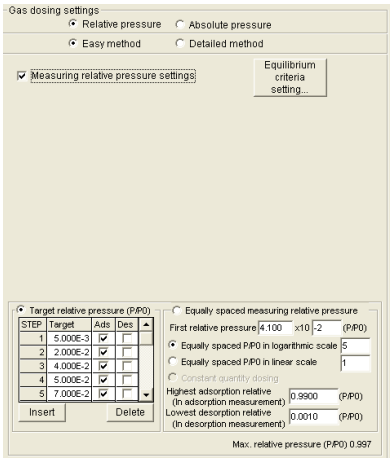
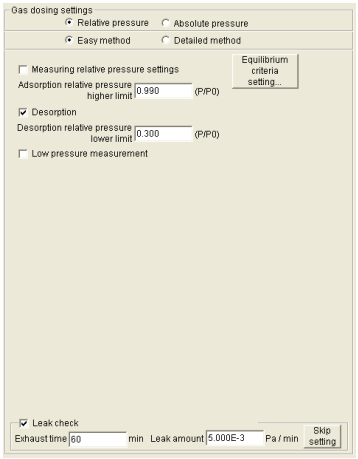
■ Setting the dosing pressure

1. Specify the adsorptive dosing pressure. Desired adsorption isotherm can be designed by specifying the dosing rate appropriately.

2. Specify the items related to the dosing pressure.

Relative / Absolute pressure indication	When the “Relative pressure” indication is selected, entries and indications are in P/P_0. When the “Absolute pressure” indication is selected, entries and indications are in kPa. 
Quick /Easy / Detailed method	When easy method is selected, setting can be accomplished easily without detailed condition setting of “target relative (absolute) pressure”, “excessive introduction amount” and “increase and decrease allowance of adsorption amount”. When detailed method is selected, setting of “target relative (absolute) pressure”, “excessive introduction amount” and “increase and decrease allowance of adsorption amount” becomes possible. Conducting detailed setting in accordance with necessary data enables to obtain data that better fit the purpose. 

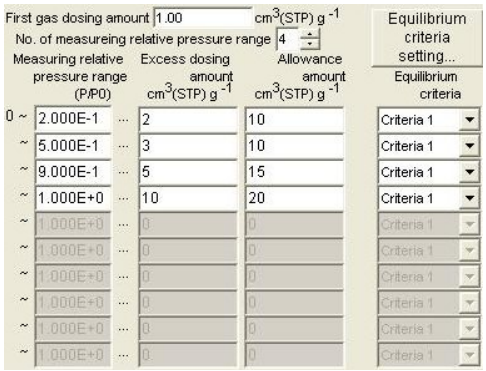
3. When “Easy method” is selected, specify the associated items as follows.

Measuring relative pressure settings	When this is checked, “Measuring relative pressure in adsorption measurement” and “Measuring relative pressure in desorption measurement” can be specified. When not checked, a predetermined value is used.	
Adsorption relative pressure higher limit (P/P_0)	Enter the adsorption higher limit in relative pressure P/P_0.	
Desorption measurement Desorption relative pressure lower limit (P/P_0)	When performing the desorption measurement, check the box. Enter the desorption lower limit in relative pressure P/P_0.	
Low pressure measurement	When “Low-pressure measurement” is checked, measurements from relative pressure of 1E-8 are carried out in N_2-77K measurements. In the case of absolute pressure, measurements from “Saturation vapor pressure x 1E-8” Pa are carried out.	

Check the low pressure measurement to perform micro-pore examination, analyze new analysis method (NLDFT/GCMC method). Untick the the low pressure measurement to perform steam adosorption measurement, analyze old classical analysis (t method, BJH method etc…).

4. When “Detailed method” is selected, specify the associated items as follows.

When the “Absolute pressure” indication is selected, assume the “relative pressure” as “absolute pressure”, and “P/P_0” as “kPa”.

Initial dosing rate $cm^3(STP)\cdot g^{-1}$	Specify the initial dosing rate (initial dosing rate for the 1st measurement point). 	
Number of measuring relative pressure range	Specify the number of “Measuring relative pressure range”.	
Measuring relative pressure range (P/P_0)	Specify the “measurement relative pressure range”.	
Excess dosing amount $cm^3(STP)\cdot g^{-1}$	In the adsorption/desorption process, the dosing pressure is determined so that it reaches the “target relative pressure” specified. With this calculation, however, dosing or exhausting gas may be repeated numerous times. For this reason, specify this excess dosing amount, which is added to or subtracted from the dosing amount calculated from the target relative pressure.	
Allowance amount $cm^3(STP)\cdot g^{-1}$	When the difference in adsorption between the previous and current measurement points exceeds this value, the current point is measured as an adsorption point, and plotted on a graph, even if the equilibrium pressure does not reach the target relative pressure.	
Equilibrium judgement	Select “Judgement 1 to 5” using ▼. Judgement is based on the following equilibrium judgement settings.	
Equilibrium judgement setting button	When this button is selected, the following “Equilibrium condition settings” window appears.	

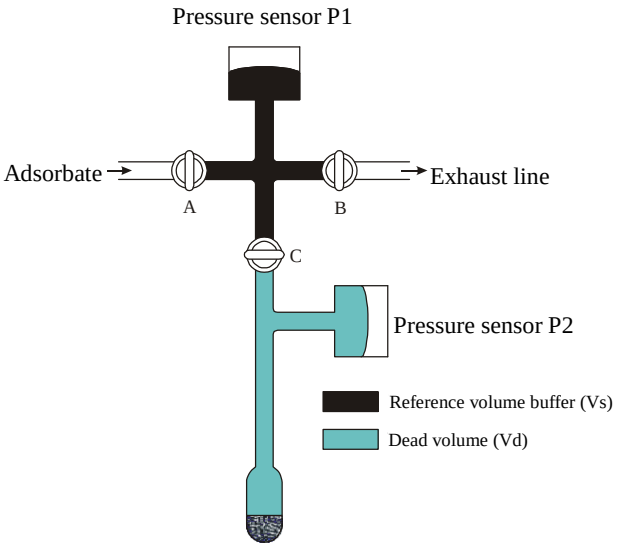
～ About excess dosing amount and allowable amount ～

1. Adsorption calculating procedure (Abridged edition)

Before describing the excess dosing amount and allowable amount, the following section describes the adsorption calculating procedure.

1. As shown in the figure on the right, the pressure sensor P1 and P2 is mounted to the "reference volume buffer: Vs" and "dead volume: Vd"
in the system, respectively.

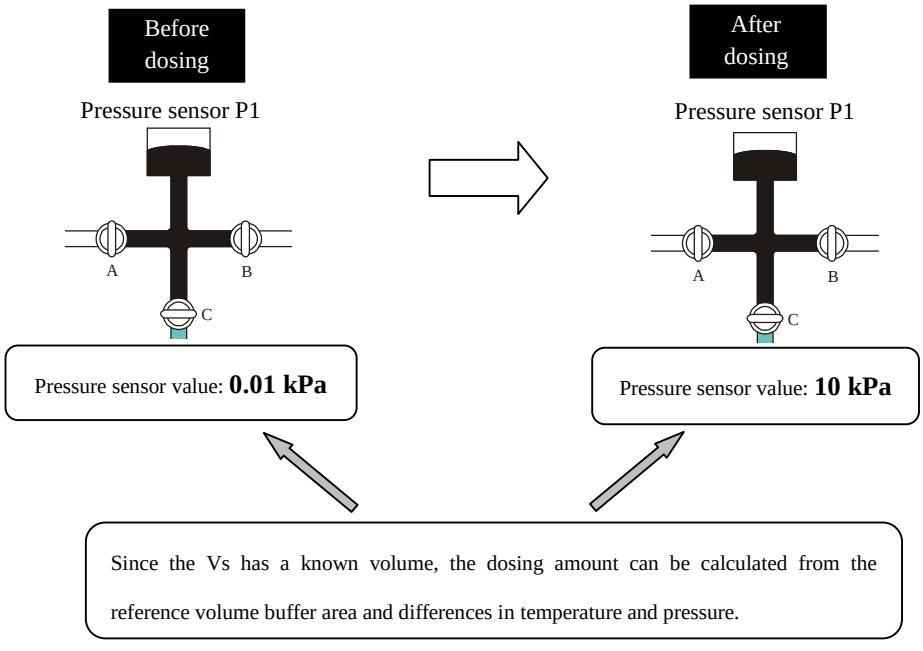
- Vs: This volume buffer has been measured at factory prior to shipment and is specific to the system.
- Vd: Since the volume of sample cell varies with each measurement, this volume must be measured using helium gas.



2. To perform the adsorption measurement, thoroughly exhaust gas from the space of Vs and Vd.

3. Dose the adsorption gas only in the space of Vs. The gas amount n_{Vs} dosed in the space of Vs can be calculated from pressure sensor values before and after dosing. (At this stage, the space of Vs is in a vacuum state.)

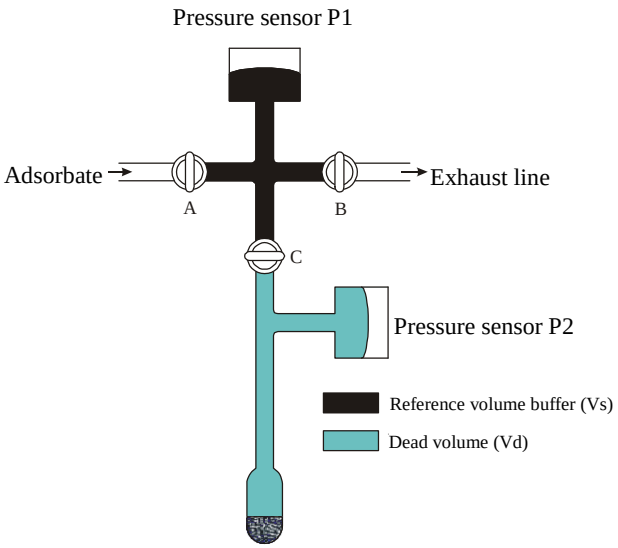
Example 1:



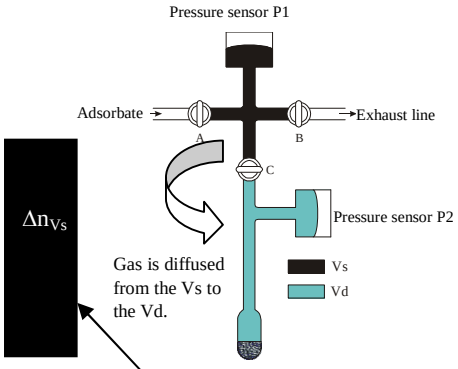
4. Open the valve C. Since the space of Vd is in a vacuum state, the suction gas in the Vs area flows into the space of Vd.

5. Close the valve C. Following the same procedure as that for Step 3, it can be measured how much the gas Δn_{Vs} has reduced.

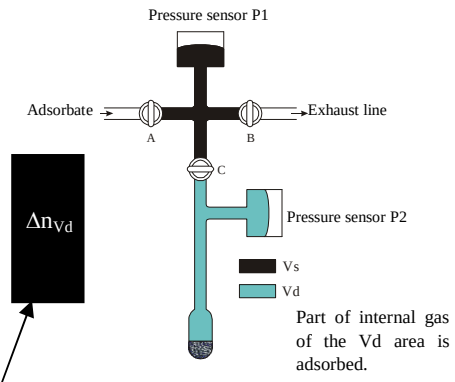
6. For the space of Vd, it can be calculated how much the gas amount Δn_{Vd} has entered according to the same procedure as that for the space of Vs.



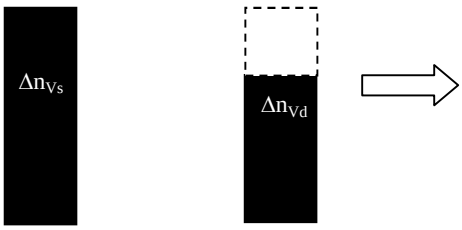
7. Normally, Δn_{Vs} calculated in Step 5 corresponds to Δn_{Vd} calculated in Stop 6. However, if adsorption takes place in the space of Vd, the pressure value will decrease, thus resulting in decreased Δn_{Vd}. The adsorption has been calculated according to differences between these Δn_{Vs} and Δn_{Vd}.



Gas amount Δn_{Vs} reduced by dosing gas in the Vd area



Gas amount Δn_{Vd} remaining after adsorption by dosing gas in the Vd area



It indicates that a difference in this gas amount adsorbs the sample cell.

Δn_{Vs}

Reduced gas amount in the reference volume buffer area

Δn_{Vd}

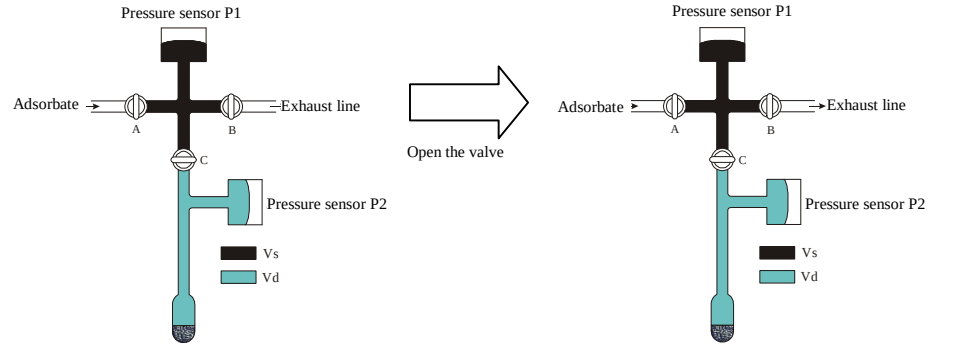
Increased gas amount in the sample cell area

2. Targeted relative pressure (Absolute pressure)

Perform the actual measurement as follows in order to automatically proceed with adsorption (desorption).

1. Determine the amount of gas to be dosed in the space of Vs first. Dose gas in the Vs area so that pressure in the space of Vd will come to a value set with the measurement parameter "Targeted relative pressure (Absolute pressure)".

Example 2: Suppose that the volume of the space of Vs is the same as that of the space of Vd and each space is in a vacuum state. In such case, consider a case where the parameter "Targeted relative pressure" is set to 10 kPa.



Dose a 20 kPa gas in the space of Vs.

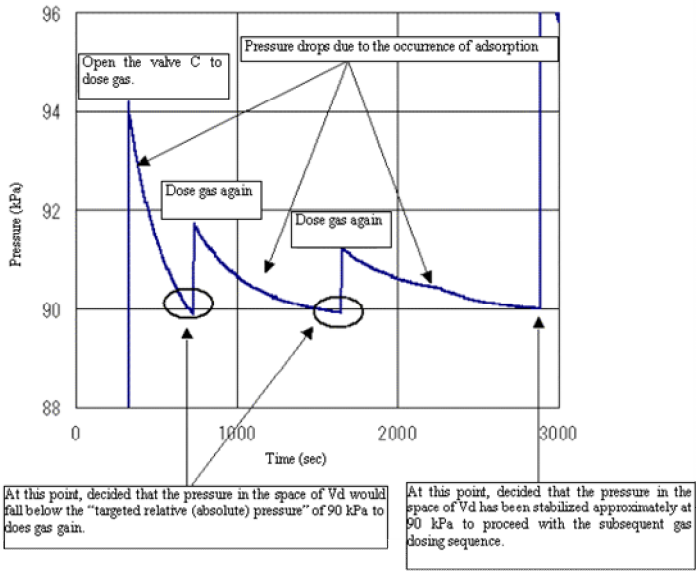
The pressure sensor P1 reads 10 kPa.

In this case, the amount of gas to be dosed in the space of Vs comes to 20 kPa.

2. The example shown above does not take into account a case where adsorption (a pressure drop) occurs in the space of Vd. When adsorption occurs, pressure in the space of Vd will drop to below the set "targeted relative (absolute) pressure". Consequently, the pressure is adjusted so that when the pressure in the space of Vd drops to below the set "targeted relative (absolute) pressure", the suction gas will be dosed again to raise the pressure to the "targeted relative (absolute) pressure". This adjustment is repeated until the pressure in the space of Vd reaches the "targeted relative (absolute) pressure".

Example 3: The following section shows pressure changes in the space of Vd at the time of adsorption measurement in the case where the parameter "Targeted relative (absolute) pressure" is set to 90 kPa.

∗Pressure stabilization for adsorption and desorption measurement can be set with the measurement parameter "Equilibrium".



3. Excess dosing amount

Example 3 shown above indicate that the system has dosed gas and waited for temperature stabilization three times to collect isothermal data at a single point, thus taking approximately 2,500 seconds to collect data at a single point. The excess dosing amount is a parameter used to increase the amount of gas dosed in the space of Vd and accelerate the measurement.

Gas dosed in the space of Vd when the "Excess dosing amount setting" parameter is set to "Disabled":

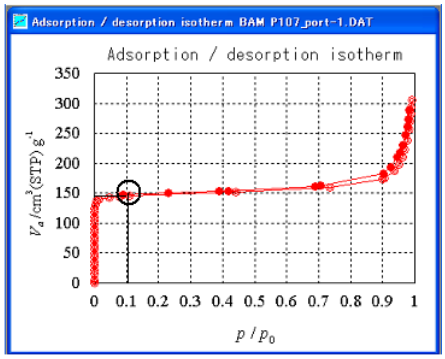
Dose gas only by the amount of gas dosed to set pressure in the space of Vd to the "targeted relative (absolute) pressure in the space of Vd.

Gas dosed in the space of Vd when the "Excess dosing amount setting" parameter is set to "Enabled":

Does gas by the amount of gas dosed to set pressure in the space of Vd to the "targeted relative (absolute) pressure + excess dosing amount in the space of Vd.

While gas was dosed three times in the case of the Example 3 shown above, using the excess dosing amount requires dosing of gas just one time to facilitate measurement.

Example 4: Suppose that you want to collect isothermal data at a point with P/P_0 of "0.1" for a sample that can obtain the isotherm shown below.



Set the "Targeted relative (absolute) pressure" parameter to "0.1" first. According to the isotherm, adsorption at relative pressure of 0.1 is approximately 150 cm^3 g^{-1}. Therefore, set the "Excess dosing amount" parameter to 150 cm^3 g^{-1}. Thus, data at the point having relative pressure of approximately 0.1can be collected in a shorter period of time without repeating dosing of gas as shown in Example 3.

Cautions:

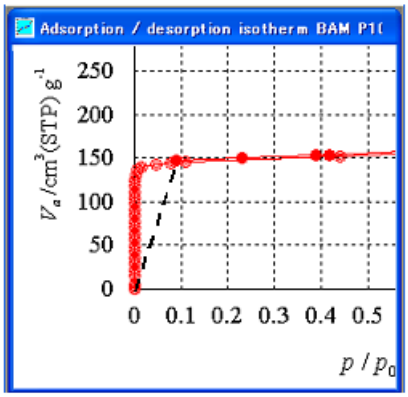
・With the example shown above, when the "Excess dosing amount" parameter is set to "250 cm^3 g^{-1}", even if the "Targeted relative (absolute) pressure" parameter is set to "0.1", a point with approximately 0.95 P/Po will be taken as the adsorption point. To avoid that, do not enter a value exceeding the adsorption at the "targeted relative (absolute) pressure" at which you want to collect the isothermal data in the "Excess dosing amount" parameter.

・The excess dosing amount is difficult to be set unless the adsorption of a sample, the shape of adsorption/desorption isotherm, and others can be forecast. For entirely unknown samples, make measurement using the "Abridged measurement procedure" and set measurement parameters as appropriate to make remeasurement.

4. Allowable amount

The allowable amount is a parameter used to set intervals to determine measurement points to the vertical axis of the adsorption isotherm ($cm^3\ g^{-1}$).

Example 5: Suppose that the first point of the "Targeted relative pressure" has been set to "0.1" and the "Allowable amount" parameter to "10 $cm^3\ g^{-1}$" for samples that can obtain isotherm shown on the right. Since the adsorption at the "targeted relative pressure" of approximately 0.1 is approximately 150 $cm^3\ g^{-1}$, 15 points (150/10=15) will be taken as the adsorption points before the "targeted relative pressure" reaches "0.1".

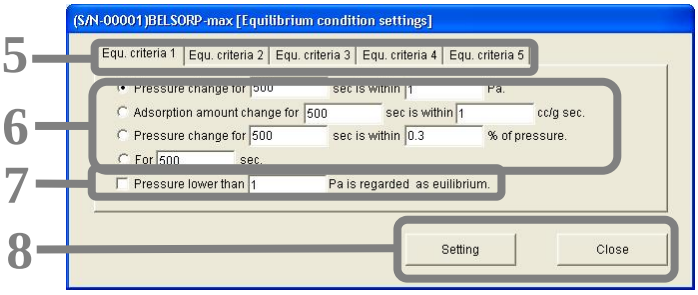


In contrast, in the case of the Type-I isotherm shown on the right, when the "Allowable amount" parameter is not set and the first point of the "Targeted relative pressure" parameter is set to "0.1", the isotherm becomes a straight line (black dotted line) up to "0.1", causing a deviation from the original isotherm.

Caution

・If the "Excess dosing amount" parameter is set to a value larger than that set with the "Allowable amount" parameter, isothermal points cannot be taken at intervals set with the "Allowable amount" parameter. As a guideline, enter a value equivalent to 50 to 80 % of the value set with the "Allowable amount" parameter as the "excess dosing amount".

5. When the Equilibrium judgement setting button is selected, the "Equilibrium condition settings" window appears as shown on the right. Select "Equ. criteria 1 to 5."

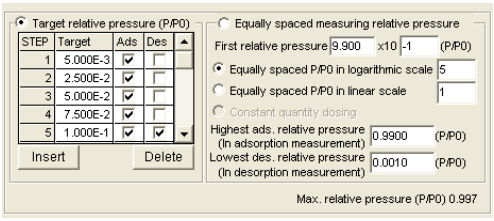


6. Select one of the conditions out of "Pressure change (Pa)", "Adsorption amount change (cc $g^{-1}\ s^{-1}$) ", "Pressure change (%)", or "without condition". Enter the equilibrium time (sec) and the change limit.

7. When the pressure below a certain level is regarded as equilibrium, enter the pressure and check in the box.

8. Select the [Setting] button. Or, select the [Close] button to close the window without setting any item. Return to the [Measurement parameter settings] window for additional setting.

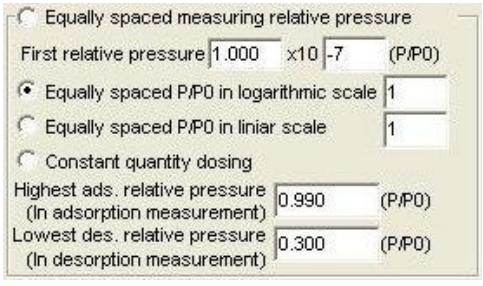
9. Select any one of “Target relative pressure” or “Equally spaced measuring relative pressure”, “Constant quantity dosing”.

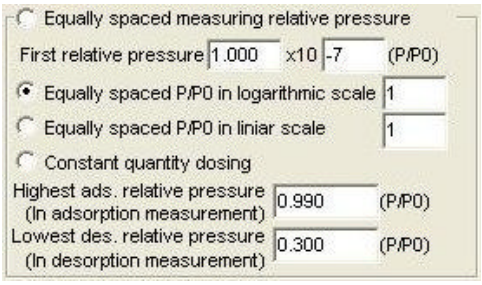


10. When “Target relative pressure” is selected, specify the associated items as follows.

Target relative pressure (P/P_0)	Specify the “target relative pressure” in the adsorption measurement.	
Adsorption	When checked, the target adsorption relative pressure on the line is effective.	
Desorption	When checked, the target desorption relative pressure on the line is effective.	
Insert	Press the [Insert] button to insert a line of step. It can be added up to 99 steps.	
Delete	Press the [Delete] button to delete a line of step. It is can be deleted to a single step.	

11. When “Equally spaced measuring relative pressure” is selected, specify the associated items as follows.

First relative pressure (P/P_0)	Enter the relative pressure to start adsorption. The adsorption points are equally spaced from the first relative pressure to the highest adsorption relative pressure.	

Equally spaced in logarithmic scale Equally spaced in linear scale Constant quantity dosing	Select one. For the equally spaced in logarithmic scale, and the equally spaced in linear scale, enter the number of adsorption/desorption points. With "equally spaced in logarithmic scale", the specified numbers of adsorption/desorption points are equally spaced in a logarithmic scale. With "equally spaced in linear scale", the specified numbers of adsorption/desorption points are equally spaced. In the "constant quantity dosing", the adsorption/desorption points reflect the first line of excess dosing amount. The lower limit of input value is "0.01".	
Highest adsorption relative pressure	Enter the highest adsorption relative pressure.	
Lowest adsorption relative pressure	Enter the lowest adsorption relative pressure. The desorption points are equally spaced from the lowest adsorption pressure to the highest adsorption relative pressure.	

12. Specify the equilibrium relative pressure allowable range.

It cannot be specified when the "Easy method" is selected.

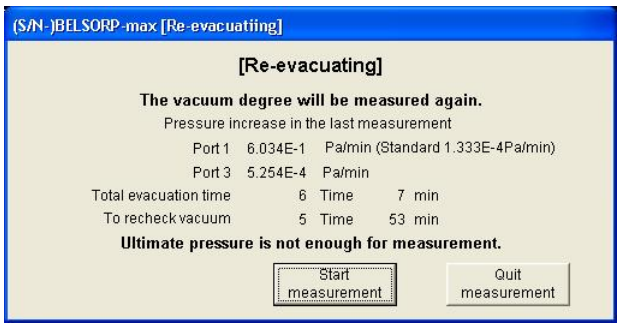
P/ P_0 tolerance (%)	Specify the allowable range to clear the target relative pressure. When the difference between the relative pressure during measurement and the target relative pressure is within the range, it clears the step and proceeds to the next step.

2. Setting the leak check

In order to check the vacuum and the amount of pressure increase in the sample portion before measurement,

check.

To measure adsorption isotherm from extremely low pressure (p/p_0 = 1E-8), be sure to do “Leak check”. In leak check, exhaust the sample cell for the specified “exhaust time”, close the valve of the sample portion, and check the amount of pressure increase. If the pressure increase is more than the specified “leak amount”, the window shown on the right is displaied, and repeats evacuation and leak check until it drops below the “leak amount”.



Setting of “exhaust time” and “Leak amount” can be changed even during leak check. Selection of Start measurement button forcedly starts measurement.

The leak check results are saved in the “VAC.CSV” file in “Send Data” folder of the “BELSORP-max” folder. Refer to the results to check the leak amount (Note that “VAC.CSV” is overwritten at every leak check).

If you check “Leak check”, “Measurement time” and “Elapsed time” are displayed on the measurement screen. They count the following times, respectively.

Measurement time·····It counts the measurement time that excludes leak check. Refer to it as an indication of time period after the Dewar vessel is filled with liquid nitrogen.

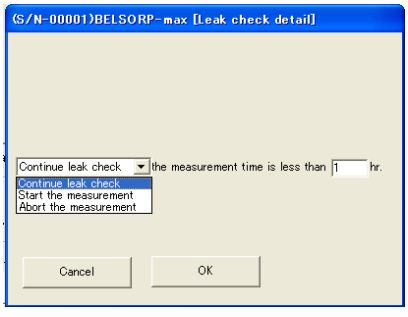
Elapsed time·····It counts the total measurement time that includes leak check.

Since measuring devices other than a dewar are set in the main unit before a leak check starts, each measuring device rises automatically if a leak check is passed successfully with a result of “Not larger than allowable pressure rise”.

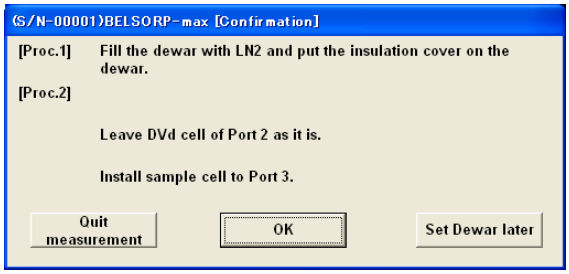
When a dewar is used and if it needs to be raised automatically after a certain time of a leak check, set the following conditions. (This function is only for dewars.)

1. Select “Leak check” on the measuring condition setting screen.

2. The window to the right appears when Detail is selected. If the leak check is not passed even when a specified measuring time (a time while the liquid nitrogen can be retained) has elapsed, select “Abort the measurement”, “Start the measurement”, or “Continue leak check”. (The selection can be changed even after the leak check starts.)

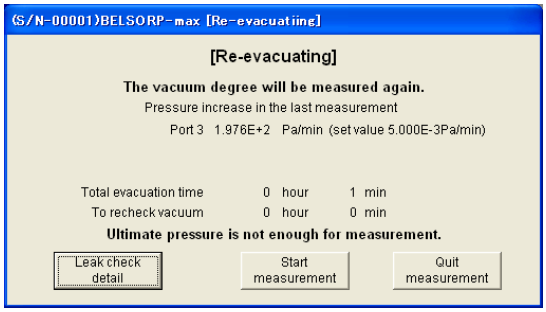


3. Set a dewar when the confirmation window to the right appears before a leak check after starting the measurement.



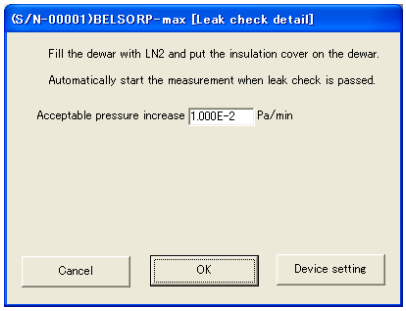
Select Set Dewar later if you set a dewar after a leak check is finished. In this case, a window appears to instruct you to set a dewar after a leak check is finished. Set a dewar following the instructions on the window.

After a leak check is started and if it is not passed with the setting value, the window below appears and the leak check is performed again.



[When a dewar is set later]

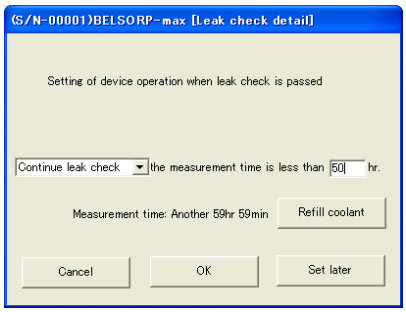
The screen to the right appears when Detail [Leak check detail] is selected.



Select Device setting if a device is set during the check. If it is selected, the screen is changed to the one shown at the right below.

[When a dewar is set from the beginning]

The screen to the right appears when Leak check detail is selected.



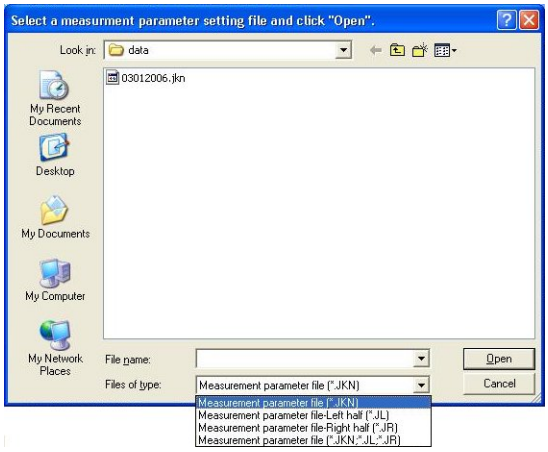
Select Refill coolant if coolant (liquid nitrogen) is replenished. The liquid nitrogen retention time (remaining time of measurement) is reset. Values, such as an allowable pressure rise value, can be changed during a leak check. A dewar having been set once can also be set again after a leak check (Select Set later).

3. Load / Save

1. Load or save the “Measurement parameter settings” file, where applicable.

Load	Select the Load button to load the existing “Pretreatment parameter setting” file. The file must have been saved using the Save button.
Save	Select the Save button to save the pretreatment parameter settings to the relevant file.

2. When you select Load or Save, the “Measurement parameter setting file” window appears. Specify the “location to load from” or the “location to save in”. Select or enter the “File name”, and then select “Open” or “Save”. An extension of “.JKN”, “.JL”, or “.JR” is automatically set to the measurement parameter setting file. For the rules to enter a file name, refer to the Windows instruction manual.



File types

Measurement parameter setting file (*.JKN):

to load or save the settings of **1. measurement parameter, 2. dosing pressure**

Measurement parameter setting file left half (*.JL):

to load or save the settings of **1. measurement parameter** on the left half

Measurement parameter setting file right half (*.JR):

to load or save the settings of **2. dosing pressure** on the right half

Limit of the measurement parameter entries

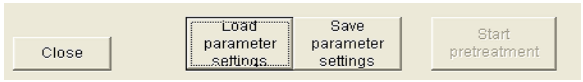
To prevent wrong measurement parameters from being entered, BELSORP-max limits parameter entry according to the instrument specification. When you attempt entering any parameter beyond the limitation, the value you entered is modified to the upper or lower limit value.

4. Starting the measurement

1. After specifying all the items, press the Start measurement button to start the measurement.

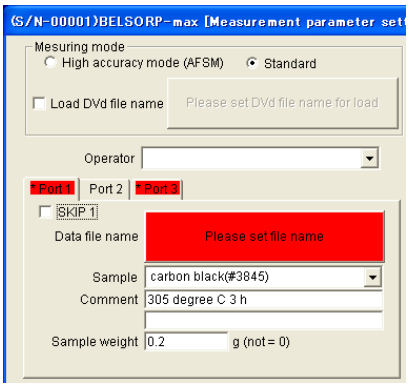
The measurement starts according to the measurement conditions predetermined in steps **1** to **3**.

When you navigate from “Pretreatment, P. 122”, select the Start pretreatment button to start the pretreatment.



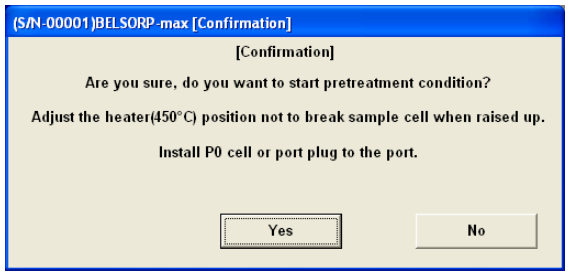
When the Start measurement button cannot be selected, there are some items remaining that must be specified (e.g. measurement data file name, etc.). Specify all the relevant items.

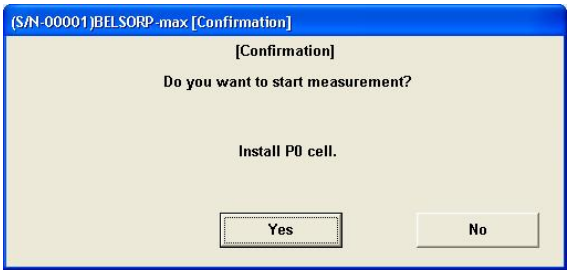
If Measurement start button cannot be selected, there are unset items. When main input items (Dvd saving file name, measurement data file name, adsorptive setting, saturation vapor pressure) are not input, items that are not input are displayed in red as shown in the window on the right. Set those items.



2. Press the Close button to cancel all the settings specified, and return to the “Main” window.

3. Select the Start measurement button. Then the “Confirmation” window (on the right) is displayed. Verify that the sample cell has been removed, and select Yes. Or, select No to return to the “Measurement parameter setting” window. After measurement is started, follow the instructions on the screen.

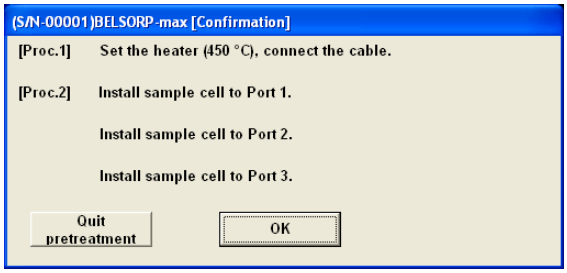




When Start measurement is selected, the “Confirmation” window (on the right) appears. Select Yes. Or, select No to return to the “Measurement parameter setting” window. After pretreatment is started, follow the instructions on the screen. You can perform continuously from pretreatment to measurement.

ooo Preparing the Dewar vessel and installing the sample cell ooo

On the “Measurement parameter setting” window, select the Start measurement button. Then, the system adjusts the pressure gauge. When the Confirmation window appears as shown on the right, prepare the Dewar vessel and install the sample cell, and then select the OK button (A similar message appears when you use the water bath, heater, or electric furnace.).



1. Preparing the Dewar vessel

⚠ The Dewar vessel is made of glass. Careful attention is required for the handling.
⚠ Do not drop the fitting into the Dewar vessel. It may be dangerous because the Dewar vessel glass may break.
⚠ Remove the ice or water adhered to the Dewar vessel and the heat insulation cap, before the sample measurement.
⚠ Do not turn on the Dewar vessel lifting-switch during the sample measurement.

1. Install the Dewar vessel to the main unit, according to “ How to install/remove the Dewar vessel, temperature measurement device P.61”.

2. Fill the Dewar vessel fully with liquid nitrogen. The Dewar vessel volume is about 2.6 L, and it retains for 60 hours.

3. After the Dewar vessel is filled with liquid nitrogen, install a heat insulation cap. Insert the Dewar vessel set pin to the set hole on the heat insulation cap.

2. Installing the sample cell

1. Install the sample cell, dead volume reference cell, and P0 cell to the measurement port according to the instruction on the "Confirmation" window.

2. Insert a glass rod to both the sample cell and the dead volume reference cell (when measuring the dead volume).

Sample cell and
Dead volume reference cell

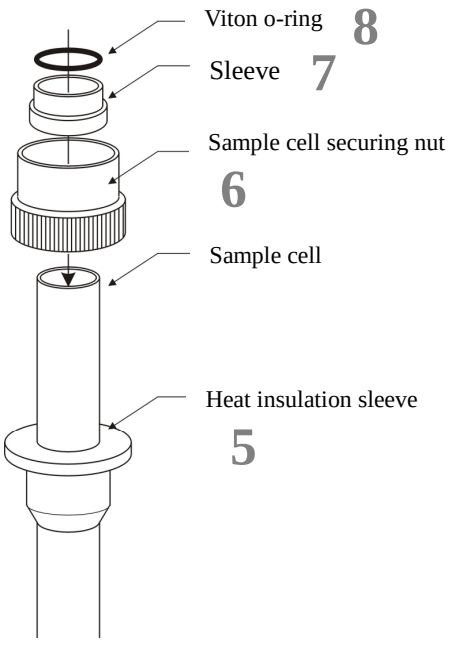
Glass rod

P0 cell (right)
o-ring (upper left)
Securing screw (lower left)

3. Install the sample cell after removing fitting and o-ring. When the sample cell is installed with the fitting still attached, it may deform the o-ring, and accordingly it may result in vacuum leakage. When you remove the sample cell from the instrument, the o-ring may remain inside the connection port. Verify that there is no o-ring inside the connection port.

4. Attach the fittings to both the sample cell and the dead volume reference cell, while paying attention not to use it upside down. Descriptions in parenthesis (< >) are for the P0 cells.

⚠ Do not drop the fitting into the Dewar vessel. It may be dangerous because the Dewar vessel glass may break.



5. Attach the heat insulation sleeve to the sample cell.

6. Attach the sample cell securing-nut <securing screw>.

7. Attach the sleeve.

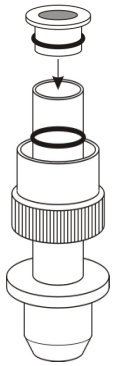
⚠ Do not use a heat insulation sleeve when using the BELSORP-max heater in the pretreatment or the measurement.

- It may result in a fire.

8. Attach a FKM (black) or FFKM (white) o-ring < o-ring >. The measurement section is sealed with this o-ring pressed on the sample cell and the measurement ports. Verify that the o-ring is not damaged, and no foreign material is pressed onto the o-ring. If air flows into the measurement section from outside, it may affect data accuracy. Replace the damaged o-ring, if any, with a new one.

9. Insert the filter (with a FKM (black) or FFKM (white) with o-ring) to the top of the sample cell.

9 Filter



10. Hold the sample cell firmly, and insert it to the sample port until it contacts the metal wall in the fitting. Tighten the sample cell securing-nut by hand.

11. Slide the heat insulation sleeve halfway down of the sample cell.

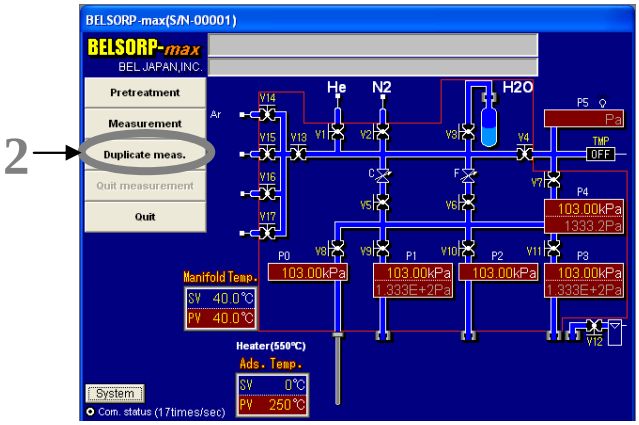
12. Set the sample cell in place, and press the OK button on the “Confirmation” window.

ooo Duplicate measurement ooo

In the duplicate measurement, continuous adsorption measurement (up to 10th) can be performed by selecting “Chemisorption measurement” or “Customized setting”. In chemisorption measurement, adsorption measurement is performed continuously with a fixed set of measurement parameters. In the customized setting, it is performed continuously with various measurement parameters.

1. Start the BELSORP-max main unit and the measurement software.

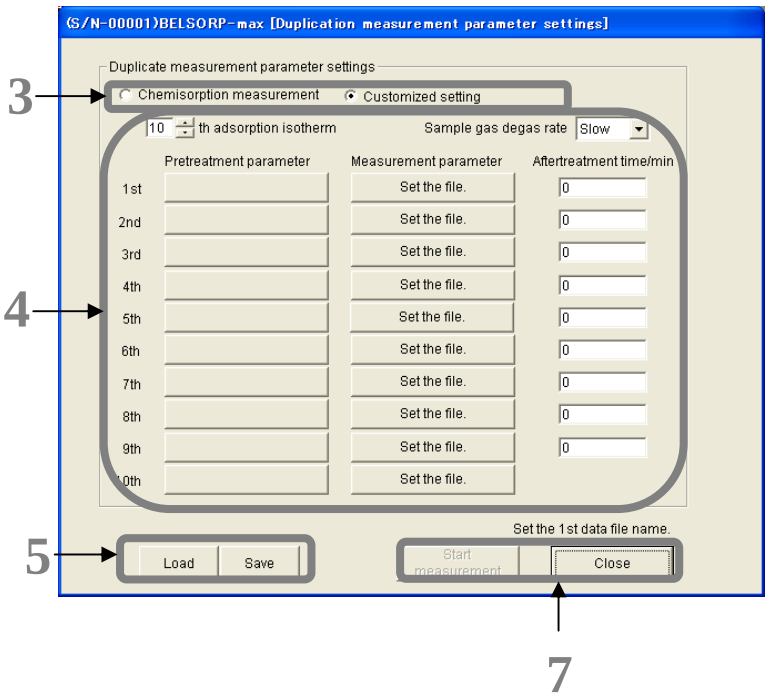
2. Select the Duplicate measurement button on the “Flow circuit diagram” window.



3. The “Duplication measurement parameter settings” window appears. Select “Chemisorption measurement” to duplicate measurement with a fixed set of measurement parameters, or select “Customized setting” to duplicate measurement while changing the measurement parameters, including the gas dosing port, adsorption temperature,leack check,dead vlume measurement, weight sample measurement etc.

When “Chemisorption measurement” is selected, specify a single set of pretreatment, measurement parameters since the measurement is duplicated with the fixed set of parameters.

When “Customized setting” is selected, specify the preatreatment, measurement parameter for every measurement of n-th adsorption. However, numebrs.of Sample cell, kind of sample cell, sample gas degas rate are fixed to these parameter selected 1st. Adsorptive becomes one choice gas either in steam.



* “Chemisorption measurement” is selected only the Dead volume measurement before measurement.

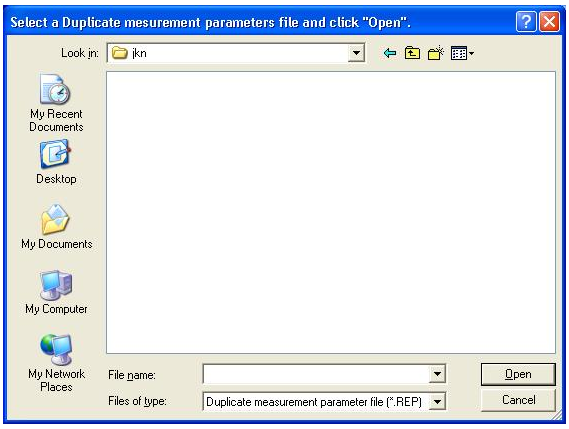
4. Set the following items.

n-th isotherm	Enter the degree of duplicated measurement, in a range of 1 to 10.
Pretreatment parameter	Specify the pretreatment parameter. Select the button on the line (degree) to specify. The “Pretreatment parameter settings” window appears. For setting, refer to “Pretreatment, P. 122”. -Button function on the “Pretreatment parameter settings” window-  Select the Load button to load the existing “Pretreatment parameter settings” file. Select the Save button to save the “Pretreatment parameter settings” file, return to the “Duplicate measurement settings” window, and associate the file with the duplicate measurement parameter. Select the Overwrite button to overwrite the “Pretreatment parameter settings” file, and return to the “Duplicate measurement settings” window to associate the file with the duplicate measurement parameter. Select the Delete button to cancel the settings, return to the “Duplicate measurement settings”, and disable the pretreatment on the line. Select the Close button to cancel the settings, and return to the “Duplicate measurement settings” window.
Measurement parameter	Specify the measurement parameter. Select the button on the line (degree) to set. The “Measurement parameter settings” window appears. For setting, refer to “Setting the measurement parameter, P. 128”. -Button function on the “Measurement parameter settings” window-  Select the Load parameter settings button to load the existing “Pretreatment parameter settings” file. Select the Save parameter settings button to save the “Pretreatment parameter settings” file, return to the “Duplicate measurement settings” window, and associate the file with the duplicate measurement parameter. Select the Overwrite button to overwrite the “Pretreatment parameter settings” file, and return to the “Duplicate measurement settings” window to associate the file with the duplicate measurement parameter. Select the Close button to cancel the settings, and return to the “Duplicate measurement parameter settings” window.
Sample gas degas rate	Select these sample gas degas trate of Sample cell.
After treatment time (min)	Specify the degassing time (minutes) after the adsorption/desorption measurement.

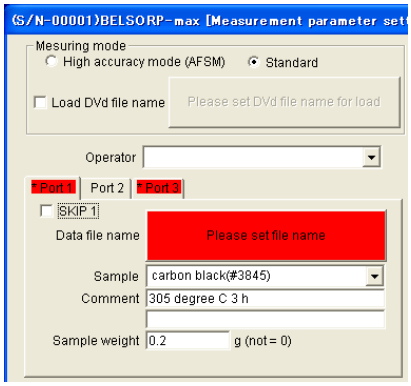
5. Load or save the “Duplicate measurement parameter settings” file, where applicable.

Load	Select the Load button to load the existing “Duplicate measurement parameter settings” file. The file must have been saved using the Save button.
Save	Select the Save button to save the duplicate measurement parameter settings to the relevant file.

6. When you select Load or Save, the “Duplicate measurement parameters file” window appears. Specify the “location to load from” or the “location to save in”. Select or enter the “File name”, and then select “Open” or “Save”. An extension of “.REP” is automatically set to the duplicate measurement parameter setting file. For the rules to enter a file name, refer to the Windows instruction manual.



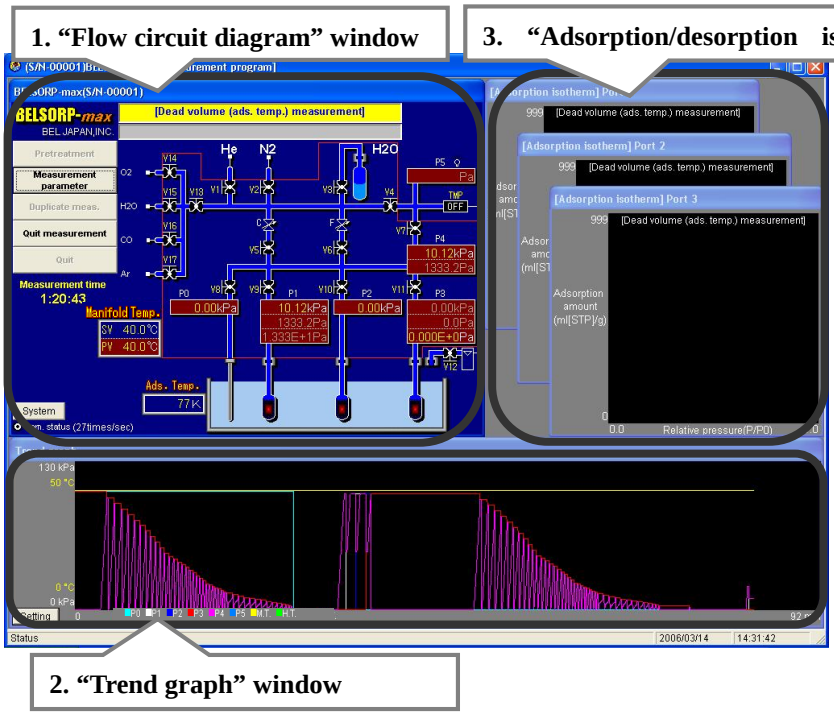
When all items are specified, use the Start measurement button to start measurement. Measurement is performed according to the measurement parameters specified in the above steps **1.** to **3.**



When the Start measurement button cannot be selected, there are some items remaining that must be specified (e.g. Dvd saving file name, measurement data file name, adsorptive setting, saturation vapor pressure, etc.). When main input items are not input, items that are not input are displayed in red as shown in the window on the right. Set those items. Specify all the relevant items. Use the Close button to cancel all the settings specified, and return to the “Main” window.

ooo “Main” window ooo

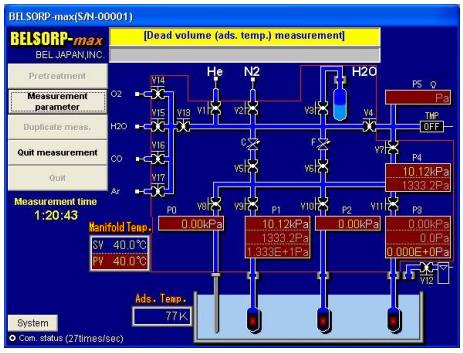
The “Main” window of the measurement software consists of the “Flow circuit diagram" window, the “Trend graph” window, and the “Adsorption/desorption isotherm" window. These windows provide information about the instrument operating status, pressure variations, measured data (adsorption isotherm), etc. in real time during the sample measurement. You can control the valve operation (V1 to V17) from the “Flow circuit diagram” window (For the stop valve operation from the “Flow circuit diagram” window, refer to P. 84.).



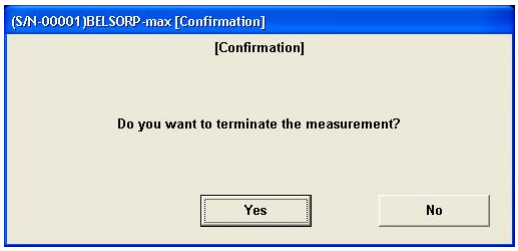
ooo “Flow circuit diagram” window ooo

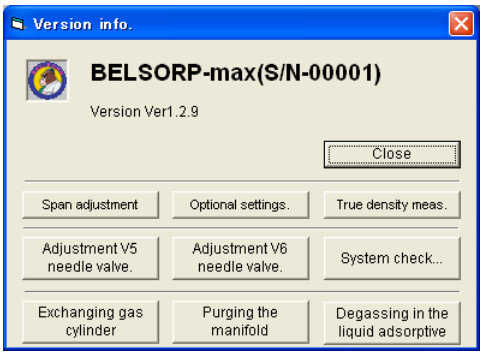
1. While measuring

The “Flow circuit diagram” window appears as shown on the right while measuring. The stop valve status, pressure, and temperature can be monitored. The buttons and their functions on the window are as follows (The stop valves can be operated manually even while measuring; however, do not do this because it may cause measurement error.).



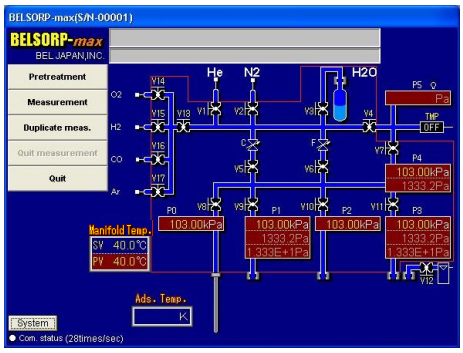
Measuring samples

Pretreatment	The pretreatment parameters can be viewed during sample pretreatment. Including “pretreatment time”, it can be changed during pretreatment. Select the Setting button to change the settings. Use the Close button to close the window.
Measurement parameter	The measurement parameters can be viewed during sample measurement. Including “dosing amount”, it can be changed during measurement. The setting range depends on the measuring status. Change the relevant items, and select the Setting button to update the settings. Use the Close button to close the window.
Duplicate measurement	The duplicate measurement parameters can be viewed during sample measurement. Including “after treatment time”, “pretreatment parameter”, and “measurement parameter”, it can be changed during measurement. Change the relevant items, and select the Setting button to update the settings. Use the Close button to close the window.
Quit measurement	Select Yes on the following “Confirmation” window to finishi the current measurement, and perform post-treatment. 

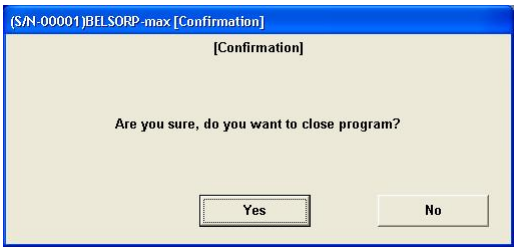
System	The software version information window appears. 

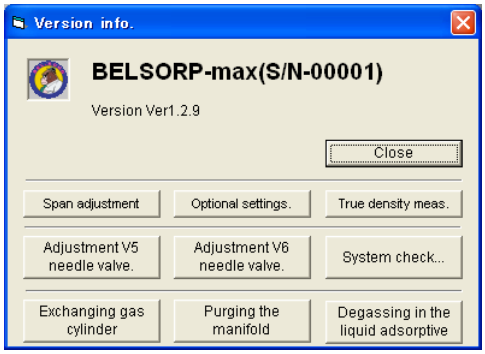
While not measuring

The “Flow circuit diagram” window appears as shown on the right while not measuring. You can control the stop valve operation. The pressure and temperature can be monitored. The buttons and their functions on the window are as follows.



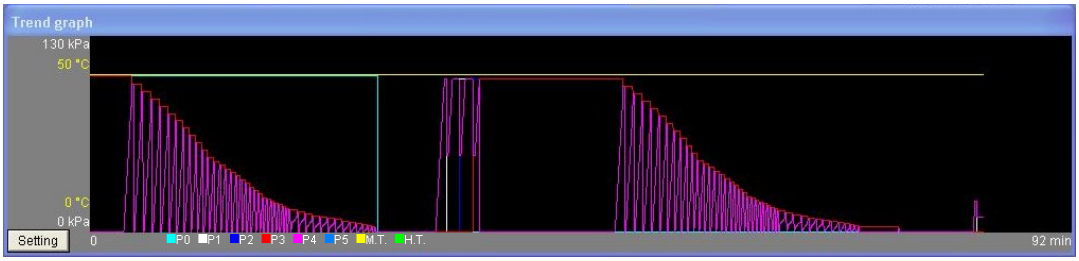
> ⚠ When you operate the valves manually, careful attention is required to prevent toxic, flammable gas from being discharged, and to prevent the turbo molecular pump from being overloaded.

Pretreatment	Select this button to pre-treat the sample. When the Pretreatment button is selected, the “Pretreatment parameter settings” window appears.
Measurement	Select this button to measure the sample. Select the Measurement button. Then the “Measurement parameter settings” window appears.
Duplicate measurement	Select this button to duplicate the measurements. When the Duplicate measurement button is selected, the “Duplicate measurement” window appears.
Quit	Select the Yes button on the following “Confirmation” window. Then, the instrument closes all valves, returns to the initial state, and then exits the software. 

System	The “System version information” window appears. For the span adjustment, refer to “Span adjustment, P. 99”. For the optional setting, refer to “Optional settings, P. 107”. For the needle valves V5 and V6 adjustment, refer to “Adjusting the needle valve, P. 97”. For the system check, refer to “System check, P. 94”. For the gas cylinder replacement, refer to “Installing and replacing gas cylinders, P.90”. For purging, refer to “Purging the tubing in the instrument, P. 101”. For degassing, refer to “Degassing adsorptive, P. 103”. 

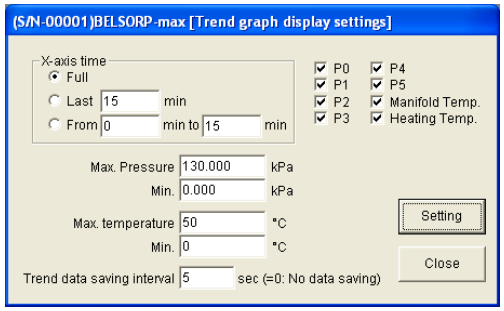
ooo “Trend graph” window ooo

Trend graphs are displayed for different pressures (P0 to P5) and temperatures (TIC1, Ads. Tmp). The pressure variations due to adsorption or desorption to/from the sample can be monitored during the sample measurement.



Buttons and their functions on the window are as follows.

Display setting	The trend graph scale can be changed. You can also set the interval to save the “TrdData.CSV” in the “BELSORP-max_SendData” folder in the “Trend data saving interval” field.



Colors used in the “trend graph” are as follows.

		Color
Temperature (M. T.)	Manifold temperature / °C	Yellow
Heating temperature (H. T.)	Temperature device / °C	Green
Pressure (P0)	Pressure at port 0 / kPa	Light blue
Pressure (P1)	Pressure at port 1 / kPa	White
Pressure (P2)	Pressure at port 2 / kPa	Red
Pressure (P3)	Pressure at port 3 / kPa	Blue
Pressure (P4)	Reference volume pressure / kPa	Purple
Pressure (P5)	Vacuum gauge / Pa (common logarithm)	Deep blue

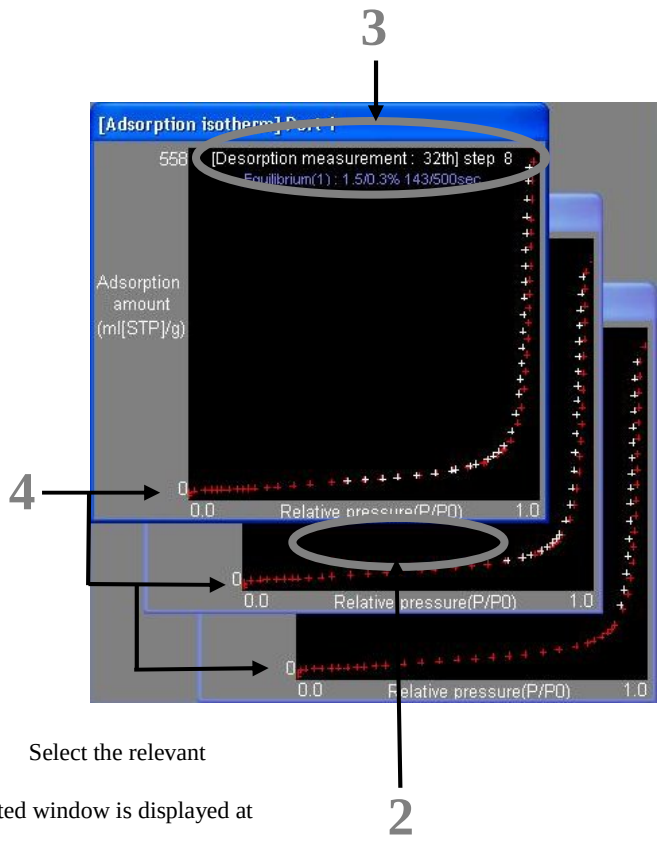
ooo “Adsorption/desorption isotherm” window ooo

1. The measured results are displayed on the “Adsorption/desorption isotherm” window during the “sample measurement”.

2. The measurement point is identified with the following colors.

- Adsorption measurement point: Red
- Desorption measurement point: White

3. The current measurement point is indicated in the message column. In the window shown on the right, it is indicated that the system is currently measuring the 32nd point in the desorption process. The step 8 corresponds to the step of “Target relative pressure” that was predetermined through the “measurement parameter Setting”.



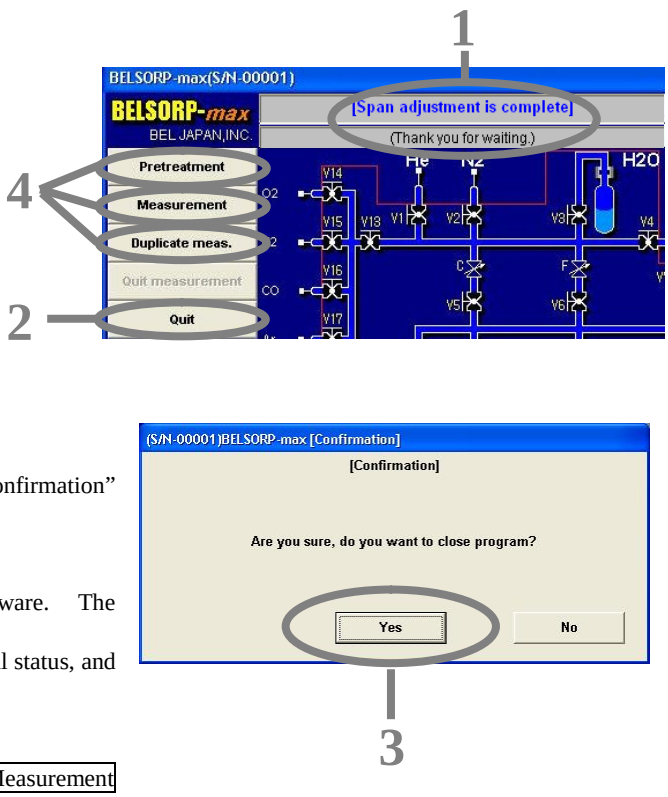
4. The results measured at Port 1 to 3 are separately displayed on the individual windows. Select the relevant window to view the measured data. The selected window is displayed at the front.

- The port 1 window is displayed when Port 1 is specified for the measurement parameter setting.
- The port 2 window is displayed when Port 2 is specified for the measurement parameter setting.
- The port 3 window is displayed when Port 3 is specified for the measurement parameter setting.

Operation to terminate the measurement

ooo Exiting the measurement software and shutdown of BELSORP-max ooo

1. Exiting the measurement software



1. When the “Sample measurement” is completed normally, the “Flow circuit diagram” window as shown right is displayed. For the “Pretreatment”, it displays a message of “Pretreatment complete”.
2. Select the Quit button, then the “Confirmation” window is displayed.
3. Select Yes to exit the measurement software. The instrument closes all valves, returns to the initial status, and then exits the software.
4. When you continue measuring, select the Measurement button. When you perform pretreatment, select the Pretreatment button. When you duplicate measurement, select the Duplicate meas button to start measuring, respectively.

2. Shutdown of BELSORP-max

In case using the instrument for the measurement, following turn-off procedure should be done more than 30 minutes after the measurement.

1. Turn off the main unit by pushing down the power switch on the back of the unit. The power indicator on the front of the main unit lights off.
2. Turn off the rotary pump immediately.
3. Close the main gas valve of a gas cylinder when the instrument will not be used for a month or more.

Caution

Do not turn off the pump with the instrument main unit turned on.

- **When the main unit remains turned on after the pump is turned off, oil may flow back and the instrument may be contaminated with the oil.**
- **We are not liable for any damages resulting from improper use of this product.**

Measurement data file

ooo Measurement data file configuration ooo

1. Measurement data

The “measurement data” of BELSORP-max is saved in a file according to each measurement step. The “measurement data” file can be opened and analyzed using the “BELSORP analysis software”, which is useful to control the measuring status.
The “measurement data” file is in the tab-deliminated text format. It can be opened using commercial spreadsheet software after measurement.

Do not open the “measurement data” file using any software except the BELSORP analysis software during measurement. Otherwise, it may prevent the measurement data from overwriting.

The “measurement data” file is saved with a name specified at measurement. An extension of “.DAT” is set to the file. An example of the “measurement data” file is shown in the following section **1.** .

When you select “After adsorption/desorption measurement” in the measurement parameter “dead volume measurement”, a file with extension of “-Z.DAT” is saved additionally (After measurement, the file corrected the dead volume with extension of “.DAT” is changed). This file contains the data before the dead volume correction.

2. Example of the measurement data file

```
==================
System property BELSORP-max Ver1.2.9
==================
"Instrument S/N:"     000002
"Vs/ml:"     31.364
==================
Measurement parameter
==================
"Adsorptive:"          H2O
"Meas. Temp./K:"     298.15
"Molecular cross-sectional area:"          0
"Molecular weight of adsorbate:"          0.00
"Equilibrium time/sec:"          0
"Measurement mode:"          2
==================
Sample information
==================
"Sample weight/g:"     0.09540
"Comment1:"          "Aerosil (Lot.0410)"
"Comment2:"          ""
"Comment3:"          "150 degree C 6 h"
"Comment4:"          "Leak amount : 0.006Pa/Min, Vacuum degree before measurement:5.469E-1Pa"
"as/m2 g-1:"          0.0000
"Molecular weight of adsorbent:"          0.00
==================
Time, dead volume
==================
"Date of measurement:"          12/01/11
"Time of measurement:"          19:23:48
"Slope of dead volume:"          5.6697E-7
"Intercept of dead volume:"          2.1205E+1
"Average dead volume:"          2.1236E+1
==================
Adsorption data
==================
"No."    "Pe/kPa"     "P0/kPa"     "Vd/ml"     "V/ml(STP)･g-1"
1          2.8403E-2    106.17       14.178      4.7988
2          6.8979E-2    106.67       14.153      10.387
3          1.1483       106.70       14.132      15.043
4          2.7673       106.46       14.122      15.935
5          5.3033       106.29       14.103      16.564
                  ⋮
0          0            0                0           0
==================
Desorption data
==================
"No."    "Pe/kPa"     "P0/kPa"     "Vd/ml"     "V/ml(STP)･g-1"
1          101.18       104.20       13.543      508.84
2          100.77       104.23       13.523      481.32
3          100.47       104.18       13.503      454.48
4          100.28       104.15       13.488      428.07
5          100.08       104.07       13.473      402.04
                  ⋮
0          0            0                0           0
```

No.: Adsorption point
Pe/kPa: Adsorption equilibrium pressure
P0/kPa: Saturation vapor pressure
Vd/ml: Dead volume change
Vd/ml(STP)*g^{-1}: Adsorption amount

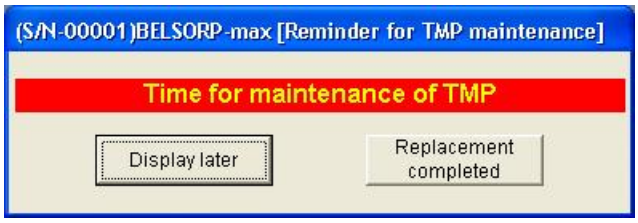
End of adsorption data

No.: Desorption point
Pe/kPa: Desorption equilibrium pressure
P0/kPa: Saturation vapor pressure
Vd/ml: Dead volume change
Vd/ml(STP)*g^{-1}: Desorption amount

End of desorption data

ooo Turbo molecular pump maintenance ooo

When the accumulated operating time of the built-in turbo molecular pump exceeds 20,000 hours, BELSORP-max prompts for maintenance on the PC screen as shown on the right. Once you select "Display later", the window will be displayed again later. Please contact our company if you find this message.



ooo Rotary pump (GHD-030) maintenance ooo

When you use the rotary pump, you must periodically replace its oil. This section describes two critical maintenance items for the rotary pump (GHD-030).

1. Replacing oil: Replace oil once every 3 months, or for every 6,000 hours operation.
2. Replacing the shaft part: Replace the pump shaft part once a year.

⚠ Failure to comply with the above periodical maintenance may result in failure of the pump, and accordingly it may cause failure of the instrument (due to backflow of oil resulted from the failure). Be sure to perform periodical maintenance as follows.

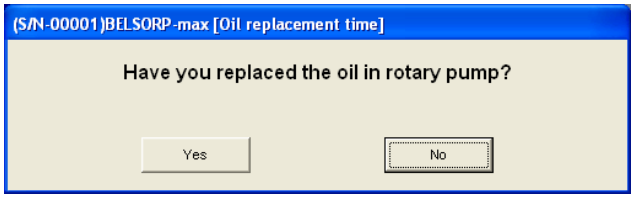
Message for oil replacement

1. Message below appears when the timing of oil replacement has come.

2. If selecting the Replace button, the message below will appear. Replace oil according to the operational procedure of "Oil replacement p. 154". After oil has been replaced, select Yes.

Select No, if oil has not been replaced. The message of step 1 will appear again.

In case of selecting the Display later button, the message above will appear again after the measurement software is started again or measurement has finished.



Replacing oil

Tools and other requisites: New oil, 6mm Allen wrench, a container for oil, towels

1. After disconnecting from the instrument hose, remove the black cap **1** as shown in the photo on the right.

> ⚠ Power is supplied to the pump through the main unit. To prevent oil from flowing back, be sure to turn off the instrument power before you disconnect the pump power cable.

2. Remove the screw **2** using a 6 mm Allen wrench. When you loosen the screw, oil may flow out. Receive the oil with a container for oil.

3. After discharging the oil completely, wipe off the oil around the drain port, and mount the screw that you removed in step **2**.

Fill new oil up to the circle marked position.

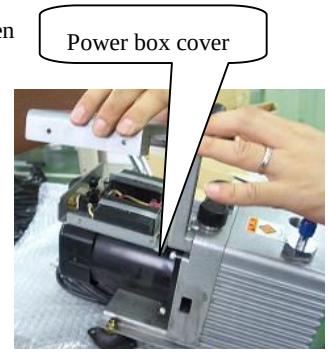
4. Fill new oil from the port **1**. Fill it up to the oil level gauge as shown in the photo on the right, which is located on the side of the pump.

5. Replace the cap **1**. Replacing oil is now complete.

> ⚠ Power is supplied to the pump through the main unit. To prevent oil from flowing back, be sure to turn off the instrument power before you disconnect the pump power cable.
>
> ⚠ When oil gets into your eye, wash it sufficiently with clean water, and obtain medical advice.
>
> ⚠ When oil contacts with your skin, wash the skin with soap and water.

3. Replacing the shaft part (spider)

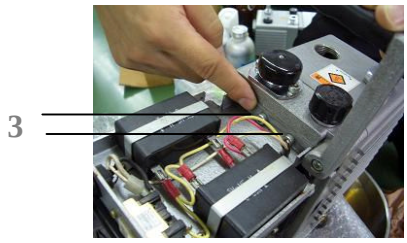
Tools and other requisites: Shaft part (spider), 4 mm, 5 mm and 6 mm Allen wrenches, Philips driver, a container for oil, towels



1. Discharge oil from the pump in the same way as described in **1. Replacing oil**, steps **1** and **2**.

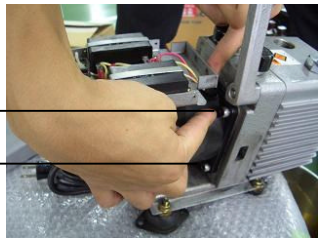
2. Remove the 4 mm screw using a Philips driver, and remove the power box cover.

3. Remove the screw **3,** using a 4mm Allen wrench.



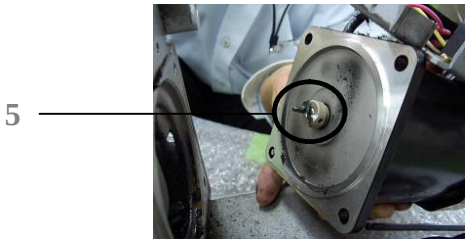
4. Remove the screw **4,** using a 5mm Allen wrench.

Once you remove the screw, the motor can be detached from the pump. Your careful attention is required.



Shaft part (spider)

5. Wipe off the dirt both on the motor and main unit, remove the shaft part (spider) at the position **5,** and then install a new spider.



6. After installing the spider, mount the pump, and then refill the pump with oil in the same way as described in **1. Replacing oil**, steps **4** and **5**. Now, replacing the spider is complete. After you refill the pump with oil, connect the pump to the main unit to check the evacuation operation.

⚠ Power is supplied to the pump through the main unit. To prevent oil from flowing back, be sure to turn off the instrument power before you disconnect the pump power cable.

⚠ When oil gets into your eye, wash it sufficiently with clean water, and obtain medical advice.

⚠ When oil contacts with your skin, wash the skin with soap and water.

ooo Daily maintenance ooo

· When power is supplied:

Verify that the power indicator lights on.

Verify that the rotary pump operates normally.

In addition, verify that the pump's exhausting noise quiets down within 1 to 2 minutes.

In the event of trouble, turn off instrument immediately, and disconnect the power cable from the wall outlet.

· Rotary pump:

Perform the appropriate maintenance to the rotary pump according to the instruction manual for the pump. In the event of any abnormal sound and/or smoke, turn off the instrument immediately, and disconnect the power cable from the wall outlet. Appropriately arrange the pump's exhaust port, i.e., connecting it to the exhaust duct, etc. .

· Power cable and communication cable:

Verify that the power cable and the communication cable are not degraded, and they are connected properly. In the event of trouble, turn off the instrument immediately, and take appropriate measures; i.e., replacing the cable, etc.

ooo Trouble shooting ooo

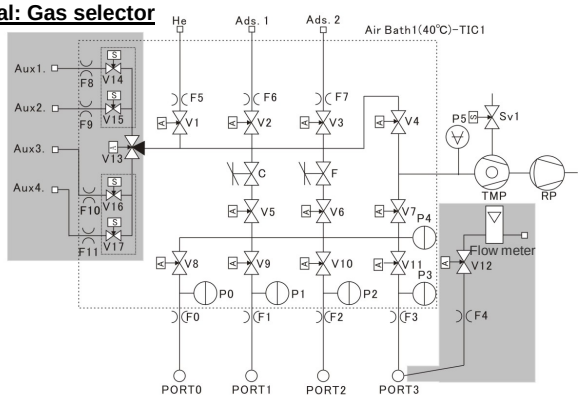
Symptoms	Check point
Power is not supplied.	・ Is the power cable connected correctly?
Insufficient vacuuming	・ Check the rotary pump operation (Is the switch on? Any trouble with oil?) . ・ Check for any loosening at the pump suction port, the connection port of the turbo molecular pump and the rotary pump. ・ When the system vacuums the sample port, check for any leakage in the sample cell, and/or any degradation of the o-ring.
The measurement system valve does not operate.	・ Is the cable connected firmly between the main unit and the computers?
The instrument stops due to communication error.	・ Is the cable connected firmly between the main unit and the computers?
Faults in adsorption amount	・ Check the purity of gas. ・ Verify that the measurement procedure is correct. ・ Measure the reference sample from Bel and verify the results.
The elevator abnormal noise	・ Grease may deteriorate. Please contact our company.
The elevator does not operate.	・ Verify that the elevator is not overloaded, and then press the elevator reset switch in the "Temperature controller pocket" on the front of the main unit.

ooo How to recover from abnormal stop ooo

If measurement is aborted after measurement is started and the Dewar vessel or the heater is lifted up for any reason (power failure, exiting software by mistake, communication failure, etc.), recover it according to the following procedure.

⚠ Moving down the Dewar vessel manually with gas charged in the sample section may cause rapid pressure increase because the sample section temperature returns to room temperature, and accordingly it may disconnect the sample cell. Be sure to comply with the following procedure.

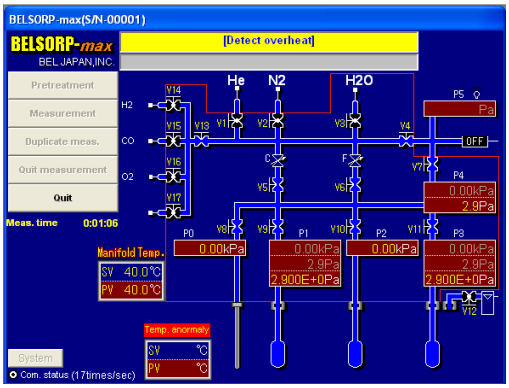
Optional: Gas selector



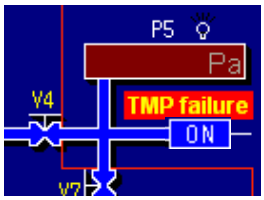
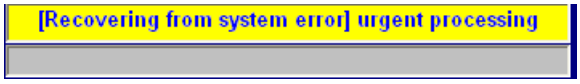
Flow diagram

The measurement stops with the Dewar vessel lifted (In case of two samples measurement).	① Exit the measurement software, and start it again. ② Open V4 to 8, and 10 (do not open V10 when the sample is installed to Port 2). ③ Close V4, 7 and 10. ④ Open V1, 5 and 6, and dose helium up to the pressure in the sample section while observing the pressure at P4. ⑤ After dosing, close all valves. ⑥ Open V9 and 11 (open also V10 when the sample is installed to Port 2). ⑦ Open V4 to 6 to exhaust slowly the sample section. ⑧ When the pressure at P4 drops below 3 kPa, move down the Dewar vessel manually. ⑨ Continue exhausting until the sample cell returns to room temperature. When it returns to room temperature, close all valves. ⑩ The procedure is now complete.
The measurement stops with the heater lifted.	① Exit the measurement software, and start it again. ② Turn off the heater switch of the temperature controller (refer to P.31). ③ Move down the heater manually. ④ Wait until the sample cell returns to room temperature. ⑤ The procedure is now complete.

ooo How to recover from error message ooo

Error message	How to reset
Temperature device overheat detection When the temperature device (450 °C heater, 550 °C heater, 1100 °C electric furnace) exceeds the specified temperature (for details refer to the temperature controller on P. 32), the temperature controller detects faults and stops heating (in such a case, the “overheat indicator” on the front of the temperature controller lights up). When the measurement software is running, it exits automatically. 	After cooling the temperature device, turn off the power switch on the front of the temperature controller, and then turn it on again to reset. Verify that the “overheat indicator” on the front of the temperature controller lights off.
Elevator overload detection When the elevator load exceeds 50 kg, it detects faults, and disables lifting operation (in such a case, the lifting switch ■ on the front of the instrument blinks red). When the measurement software is running, it exits automatically. 	A reset switch for the elevator is located in the “temperature controller pocket” on the front of the instrument. After you remove the cause, press the reset switch to release any protective actions.
System faulty pressure detection ***(Only when the measurement software is started)*** When any pressure gauge exceeds 130 kPa, it detects faults and triggers an emergency stop (exhaust process). Only in the adsorption/desorption measurement, it detects faults when P0 exceeds 110 kPa. 	Leave it without any action until the software exhausting process is complete.

Maintenance

Turbo molecular pump overload detection ***(Only when the measurement software is started)*** When air is sucked while the turbo molecular pump is in operation, it detects load and stops the TMP operation (in such a case, “TMP error” appears on the software screen). 	Even when the TMP error is indicated, the measurement is not aborted. Stop the low-pressure measurement because vacuum is degraded. To stop measuring and reset the error, turn off the instrument power switch 10 minutes or more after the error detection, and turn it on again another 5 seconds later to reset.
Recovering from system error In case measurement is stopped by some reason, urgent processing will begin at restart of the software. 	When measurement is stopped, finish the software and restart it. Leave it as it is, since urgent processing will start automatically.

ooo Consumables ooo

The following consumables are available with BELSORP-max. Please contact us for any inquiry.

model	Item and Specification
【Sample cell】	
010-20000-0-0	Pyrex sample cell (MAX.500 °C) 3/set
010-20001-0-0	Silica sample cell (1.8 ml) 1/set
010-20002-0-0	Pyrex small volume sample cell (MAX.500 °C, 0.5 ml, 200 mm) 1/set
010-20003-0-0	Silica small volume sample cell (0.5 ml, 200 mm) 1/set
010-20004-0-0	Pyrex large volume sample cell (MAX.500 °C, 0.5 ml, 200 mm) 3/set
010-20005-0-0	Silica large volume sample cell (5 ml, 200 mm) 1/set
010-20008-0-0	Pyrex flow gas sample cell (Max.500 °C,230 mm) 1/set
010-20009-0-0	Silica flow gas sample cell 1/set
010-22021-0-0	NSD capucel sample cell 1/set
010-22014-0-0	Pellet sample cell 1/set
【Others】	
010-21000-0-0	Glass rod (Pyrex sample cell, Pyrex flow gas sample cell: 010-20000-0-0,010-20008-0-0) 3/set (Pyrex)
010-21001-0-0	Glass rod (Silica sample cell, Silica flow gas sample cell: 010-20001-0-0,010-20009-0-0) (Silica)
010-21002-0-0	Glass rod for Pyrex large volume sample cell (010-20004-0-0) 3/set (Pyrex)
010-21003-0-0	Glass rod for silica large volume sample cell (010-20005-0-0) (Silica)
010-21006-0-0	Glass rod for Pyrex small volume sample cell (010-20002-0-0) 3/set (Pyrex)
010-21007-0-0	Glass rod for silica small volume sample cell (010-20003-0-0) (Silica)
010-21010-0-0	Glass rod for quick seal (010-20000-0-0) 3/set (Pyrex)
010-21011-0-0	Glass rod for quick seal (Pyrex large volume sample cell: 010-20004-0-0) 3/set (Pyrex)
010-21012-0-0	Glass rod for quick seal (Silica sample cell: 010-20001-0-0) (Silica)
010-21013-0-0	Glass rod for quick seal (Silica large volume sample cell: 010-20005-0-0) (Silica)
010-21008-0-0	Glass rod for pellet sample cel (010-22014-0-0)
010-22015-0-0	Pellet sample tube (Pellet sample cell: 010-22014-0-0)
900-00017-0-0	Sample cell heat insulation sleeve 3/set
010-22024-0-0	P0 Cell heat insulation sleeve 3/set
010-22003-0-0	Dewar vessel heat insulation lid

model	Item and Specification
【Others】	
010-22000-0-0	Sampling funnel 3/set (Pyrex)
010-22001-0-0	Liq. bottle 2/set
010-22002-0-0	P0 cell (SUS)
010-22022-0-0	P0 port cap (4 cm × 3φ)
900-00016-0-0	Sample cell cap 10/set
900-00011-0-0	Sample scattering prevention filter 6/set 20m (Viton)
900-00013-0-0	Sample scattering prevention filter 6/set 20m (Perflour)
900-20002-0-0	Sample scattering prevention filter (quick seal) 1/set (Viton)
900-20003-0-0	Sample scattering prevention filter (quick seal) 1/set (Perflour)
900-10005-0-0	Sample cell weighting stand
900-10004-0-0	Sample cell stand
900-00004-0-0	Perflour o-ring 6/set
900-00000-0-0	Viton o-ring for P0 cell (P-3) 12/set
910-00001-0-1	Corrosion resistant rotary pump (GHD-030(Fomblin oil))
910-00000-0-1	rotary pump (GHD-30)
010-10011-0-0	Dewar vessel
010-10022-0-5	Measurement site safety cover
910-20000-0-0	Standard oil for vacuum pump (1 L) 600 cc/unit (GHD-30)
SMR-100	Standard oil for vacuum pump (1 L) 600 cc/unit (Trivac, GLD-030, GLD-51)
Ultra Grade 19	Standard oil for vacuum pump (1 L) ・RV3
910-20002-0-0	Fomblin oil for vacuum pump (1 kg) (GHD-030(Fomblin oil))

Appendix

Adsorptive		Boiling point/K	Critical point/K	Temp. /K	Saturation vapor pressure/kPa*[1]	2nd virial coefficient/Pa^{-1}
Nitrogen	N_2	77.4	126.2	77.4	101.325*[3]	-4.264×10^{-7}
Argon	Ar	87.3	150.8	77.4	30.615*[6]	-4.587×10^{-7}
				87.3	101.325*[3]	-3.300×10^{-7}
				298.15	-	-6.093×10^{-7}
Methane	CH_4	111.6	190.4	298.15	24973*[4]	-1.689×10^{-7}
Ethane	C_2H_6	184.6	305.4	293.15	3553.0	-7.985×10^{-8}
				298.15	3916.2	-7.569×10^{-8}
				303.15	4301.9	-7.181×10^{-8}
Carbon dioxide	CO_2	194.7	304.1	194.7	101.325	-2.143×10^{-7}
				298.15	6444.8	-5.031×10^{-8}
Hydrogen	H_2	20.4	33.2	293.15	-	3.464×10^{-9}
				298.15	-	3.436×10^{-9}
				303.15	-	3.407×10^{-9}
Krypton	Kr	119.9	209.4	77.4	0.3310*[5]	-1.007×10^{-6}
Ammonia	NH_3	239.8	405.5	293.15	861.87*[2]	-1.217×10^{-7}
				298.15	1007.2*[2]	-1.132×10^{-7}
				303.15	1170.3*[2]	-1.056×10^{-7}
Oxygen	O_2	90.2	154.6	293.15	-	-6.845×10^{-9}
				298.15	-	-6.312×10^{-9}
				303.15	-	-5.814×10^{-9}
Nitrogen monoxide	NO	121.4	180	298.15		-3.319×10^{-9}
Carbon monoxide	CO	81.7	132.9	293.15	-	-3.530×10^{-9}
				298.15	-	-3.063×10^{-9}
n-butane	n-C_4H_{10}	272.7	425.2	293.15	208.23	-3.121×10^{-7}
				298.15	243.08	-2.950×10^{-7}
				303.15	283.14	-2.791×10^{-7}
iso-butane	iso-C_4H_{10}	261.4	408.2	293.15	300.51	-2.803×10^{-7}
				298.15	348.66	-2.652×10^{-7}
				303.15	284.18	-2.511×10^{-7}
Benzene	C_6H_6	353.2	562.2	298.15	12.778	-6.074×10^{-7}
Toluene	$C_6H_5CH_3$	383.8	591.8	298.15	3.822	-9.439×10^{-7}
Methanol	CH_3OH	337.7	512.6	298.15	17.050	4.290×10^{-7}
Ethanol	C_2H_5OH	351.4	513.9	298.15	7.958	5.429×10^{-7}
Cyclohexane	C_6H_{12}	353.8	553.5	298.15	13.100	-6.902×10^{-7}
				323.15	36.439	-5.199×10^{-7}
Carbon tetrachloride	CCl_4	349.9	556.4	298.15	15.323	-6.104×10^{-7}

ooo Physical Properties of Adsorptives ooo

*1 For the calculation of saturation vapor pressure, Antoine equation is used when 101.325 kPa or below and Wagner equation (partly Harlacher-Braun equation) is used when 101.325 kPa or above. The blank ones in the table are above the critical point.

*2 Harlacher-Braun equation is used.

*3 The saturation vapor pressure of nitrogen (77.4 K) and argon (87.3 K) is just the pressure at the boiling point. So for them, the 2nd virial coefficient at the atmospheric pressure is listed.

*4 Since carbon dioxide does not exist as a liquid state under the atmospheric pressure, the sublimation pressure is listed as the saturation vapor pressure.

*5 Krypton is solid at 77.4 K. The saturation vapor pressure is obtained from Clausius-Clapeyron equation as a super cooled liquid (ASTM D 4780-95).

*6 Argon is solid at 77.4 K. The saturation vapor pressure is obtained from Wagner equation as a super cooled liquid (Gasses & Liquids 4th Edition Robert C. Reid).

ooo Molecular diameter ooo

Adsorption		Molecular diameter(nm)*6
Nitrogen	N_2	0.364-0.37
Argon	Ar	0.355-0.36
Methane	CH_4	0.409
Hydrogen	H_2	0.268-0.269
Krypton	Kr	0.404-0.408
Oxygen	O_2	0.392-0.398

*6 T. Takaishi and Y. Sensui, 'Thermal Transpiration Effect of Hydrogen, Rare Gasses and Methane' Trans. Faraday Soc., **59**, 2511 (1963).

ooo Calculation of Saturation Vapor Pressure ooo

The saturation vapor pressure of pure substances is listed in various literatures. For instance, there are "Physical constant" edited by the society of chemical engineers, and "Physical constant of chemical engineering". In the table of physical properties of adsorptives, the saturation vapor pressure of common substances is listed. Also, Figure 1 shows the vapor pressure of water at various temperatures.

Figure 1: Saturation vapor pressure of water

θ/°C	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
0	0.611	0.657	0.706	0.758	0.813	0.872	0.936	1.002	1.073	1.148
10	1.228	1.313	1.402	1.498	1.599	1.705	1.818	1.938	2.064	2.198
20	2.338	2.487	2.644	2.810	2.985	3.169	3.362	3.567	3.781	4.007
30	4.245	4.495	4.757	5.033	5.322	5.626	5.945	6.279	6.629	6.996
40	7.381	7.784	8.205	8.646	9.107	9.589	10.093	10.620	11.170	11.745
50	12.344	12.970	13.623	14.303	15.012	15.752	16.522	17.324	18.159	19.028
60	19.933	20.873	21.852	22.869	23.925	25.024	26.164	27.348	28.578	29.854
70	31.177	32.550	33.974	35.450	36.980	38.565	40.207	41.908	43.668	45.490
80	47.376	49.327	51.345	53.432	55.589	57.819	60.123	62.503	64.962	67.501
90	70.122	72.827	75.619	78.500	81.471	84.535	87.694	90.951	94.307	97.765

* Wargner equation is used (Gasses & Liquids 4th Edition Robert C. Reid).

There are many suggested equations to estimate the saturation vapor pressure. The representative equations are: Antoine equation, Harlcher-Braun equation, and Wagner equation.

Antoine equation

This is often used when the converted temperature ($T_r = T/Tc$ where Tc is the critical temperature) is less than 0.75 and the pressure is 0.1-200 kPa. At the temperature T, the saturation vapor pressure P_0 is expressed as the following with the constant A, B, and C:

$$\log P_0 = A - \frac{B}{C + T[\mathrm{K}]}$$

Wagner equation

McGarry compared 8 vapor pressure equations and found out Wagner equation is the best estimation of vapor pressure up to the critical point. At the temperature T, the saturation vapor pressure P_0 is expressed as the following with the constant A, B, C, and D:

$$\ln(P_0 / P_c) = (Ax + Bx^{1.5} + Cx^3 + Dx^6)/(1-x)$$

where

$$x = 1 - T/T_c$$

and T_c and P_c are the critical temperature and critical pressure respectively.

Harlcher-Braun equation

This equation estimates the vapor pressure well from the boiling point to the critical point. At the temperature T, the saturation vapor pressure P_0 is expressed as the following with the constant A, B, C, and D:

$$\ln P_0 = A + B/T[\mathrm{K}] + C\ln(T[\mathrm{K}]) + \frac{DP_0}{(T[\mathrm{K}])^2}$$

The constants are listed in the Chemistry handbook or other references.

There are many other equations suggested to estimate the saturation vapor pressure, but the estimation values do not necessarily coincide with the actual values.

Reference:

R.C. Reid, J.M.Prausnitz and B.E. Poling, "The Properties of Gases & Liquid", 4th ed. McGraw-Hill, Inc.

ooo Calculation of the 2nd virial coefficient ooo

In the volumetric method, the volume of adsorption is determined by using the ideal gas equation. The virial coefficient allows us to correct for the nonideality of real gases. By using the 3rd and 4th virial coefficient, it is possible to perform correction in the wide range of pressure, but here, the calculation of 2nd virial coefficient is discussed in detail. If you want to calculate the 3rd and 4th virial coefficient, please refer to other scientific sources since there should be plenty of information in them. Please enter B_p (Pa^{-1}) value to correct for the nonideality.

For single component gases, the 2nd virial coefficient is calculated by using the following equations:

$$\frac{BP_C}{RT_C} = B^{(0)} + \omega B^{(1)} + B^{(2)}$$

$$B^{(0)} = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^{(1)} = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$B^{(2)} = \frac{a}{T_r^6} - \frac{b}{T_r^8}$$

$$T_r = \frac{T}{T_C}$$

$B^{(2)}$ is the term for polar molecules. This is reported by Tsonopoulos. a, b cannot be determined accurately, so they are only classified into some values.

Class	Compound	a	b
1	Ketenes, aldehydes, nitrides, Ethers, NH_3, H_2S, HCN, esters	$-2.112 \times 10^{-4}\mu_r - 3.877 \times 10^{-21}\mu_r^8$	0
2	Mercaptans	0	0
3	Monoalkyhalides	$2.076 \times 10^{-11}\mu_r^4 - 7.048 \times 10^{-21}\mu_r^8$	
4	Alcohols	0.0878	0.04-0.06
5	Phenol	-0.0136	0

μ_r in the table is determined by the following equation:

$$\mu_r = \frac{10^5 \mu^2 P_C}{T_C^2}$$

P_C : Critical pressure / bar

T_C : Critical temperature / K

μ : Dipole moment /debyes

ώ :Acentric Factor (Asymmetry factor for molecules)

Reference:

R.C. Reid, J.M.Prausnitz and B.E. Poling, “The Properties of Gases & Liquid”, 4th ed. McGraw-Hill, Inc.

ooo Pretreatment ooo

Pretreatment is performed to remove water and other molecules adsorbed on the surface of adsorbent and inside pores (for the pretreatment of chemisorption, it might involve the chemical reactions at the surface, e.g. oxidation and reduction).

As the pretreatment method:

1.Heat the sample under the flow of inactive gas (nitrogen, helium, etc.)

2.Heat the sample while in vacuum

In case of method 1, the structure of pretreatment instrument can be simple, but the heating time needs to be longer than method 2. Also, when cooling down the sample to the room temperature under the flow of gas, the impurities in the gas might re-adsorb inside the pores if the sample has micropores. If it happens, it influences the measurement badly. Pay attention to the purity of the gas you use. In case of method 2, it is generally enough to vacuum with a rotary pump (1 Pa). If you need to measure the adsorption isotherm at 10^{-2} Pa or less to analyze the pore size distribution with DFT theory or simulation, you need to achieve the better vacuum by using a turbo-molecular pump.

The higher temperature pretreatment is performed, the more efficient it can remove impurities. However, it is important not to change the structure of sample by putting too much heat. Ideally, one can investigate the effect of temperature increase to the sample by using a thermogravimetric balance. If the temperature cannot be set high (e.g. pretreatment of polymer materials), the pretreatment time needs to be longer. Carbon material does not change its structure even at high temperature. In case of active carbon, water molecules cannot be desorbed from the pores unless the temperature is high. Generally, pretreatment is performed at about 573 K. It is the same for zeolite, but the temperature needs to be increased gradually to avoid the structure change of pores by the thermo-hydration reaction.

The table below lists the typical pretreatment temperature of common substances. Determine the pretreatment temperature after considering the physical properties and surface characteristics of the substance you actually measure.

	Pretreatment temp. /°C	Remarks
Active carbon	150-500	There is possibility that surface functional groups desorb at 300 °C or higher, but it does not affect the surface area and properties of pores so much.
Zeolite	300-500	If performing the measurement from extremely low pressure, pretreatment needs to be performed for 5 hours or longer under the high vacuum.
Polymer	r. t. -100	If the temperature cannot be increased, it takes longer time for pretreatment.
Alumina	100-150	At 150 °C or higher, the surface hydroxyl might be condensed or dehydrated.
Silica	100~150	At 200 °C or higher, the surface hydroxyl might be condensed or dehydrated.
Titania	100-500	By heating under the vacuum, it might produce reducing atmosphere and the surface area might be changed because of desorption of oxygen at the surface. It is desirable to perform pretreatment under the flow of high purity air or oxygen.
Calcium carbonate	200-400	It is thermally decomposed around 900 °C.
Cement	100-120	Because of the hydrate, dehydration reaction occurs during the high temperature pretreatment.

BEL JAPAN,INC.

BELSORP

High precision gas / vapor adsorption apparatus

User's Manual

(BELMaster™/BELsim™)

Ver.2.3.1

BELSORP-max

BELSORP-mini

BELSORP-aqua3

BELSORP-HP

BELSORP-28SA/18SA/18PLUS

BELSORP series

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Precautions

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Preparations for using the BELSORP analysis program

Chapter 1: Introduction

This is a data analysis program designed to analyze the datameasured by the BELSORP series of adsorption measurement apparatuses. This program reads the data files that were measured using a BELSORP measuring instruments, and can then display graphs and numerical data. The analysis data can be printed and saved.

1-1. BELSORP analysis program

The following sample information about surface areas and pores can be obtained from the measured data.

Name of analysis	Adsorptive	Analysis method	Primary data produced
Adsorption / desorption isotherm	Istotherms are displayed with this analysis. Judging from the shape of isotherm, the characteristic of the sample can be seen and appropriate method to analyze the isotherm can be chosen.		
PCT curve	H_2	Change in amount of hydrogen storage capacity	Amount of hydrogen storage capacity
BET plot	N_2, Ar, Kr, etc.	Evaluates a specific surface area for physical adsorption	Monomolecular layer adsorption
Langmuir plot	O_2, etc.	Evaluates the amount of chemical adsorption	Monomolecular layer adsorption
t plot	N_2	Evaluates micropores	Total specific surface area, external specific surface area, and pore volume
α_s plot	N_2	Evaluates micropores	Total specific surface area, external specific surface area, and pore volume
MP plot	N_2	Micropore distribution curve	Micropore distribution
BJH plot	N_2	Mesopore distribution curve	Mesopore distribution, volume and area
CI plot	N_2	Mesopore distribution curve	Mesopore distribution, volume and area
DH plot	N_2	Mesopore distribution curve	Mesopore distribution, volume and area
INNES plot	N_2	Mesopore distribution curve	Mesopore distribution, volume and area
DA plot	N_2, CO_2, C_6H_6, etc.	Evaluate the micropore volume	Micropore volume
HK plot	N_2, Ar	Micropore distribution curve	Micropore distribution (Pore shape: Slit)
SF plot	N_2, Ar	Micropore distribution curve	Micropore distribution (Pore shape: Cylinder)
Isosteric heat of adsorption	H_2O, etc.	Evaluates differential heat of adsorption	Differential heat of adsorption
Difference of adsorption isotherms	H_2O, NH_3 , etc.	Evaluates the amount of chemical adsorption	Difference adsorption isotherm
Metal dispersion	H_2, CO, etc.	Evaluates metal dispersion	Metal dispersion
Molecular probe	CO_2, C_2H_6, n-C_4H_{10}, iso-C_4H_{10} , etc.	Evaluate micropores	Micropore distribution curve
NLDFT/GCMC	N_2, Ar, CO_2	Evaluate micropores and mesopores	pore distribution curve

1-2. Required computer environment

This program can be used with the following systems and conditions.

<table>
<tr><th colspan="5">[Personal computer]</th></tr>
<tr><td></td><td colspan="4">Required system environment</td></tr>
<tr><td rowspan="2">Operating system</td><td>Microsoft Windows® 7
(32 bit / 64 bit)
Home Basic or Home Premium or more</td><td>Microsoft Windows®
Vista
Service Pack 2 or more</td><td colspan="2">Microsoft Windows® XP
Home or Professional Edition
Service Pack 2 or more</td></tr>
<tr><td colspan="4">(Any computer that can run the English version of these OS)</td></tr>
<tr><td>CPU</td><td colspan="4">Intel processor</td></tr>
<tr><td>Memory</td><td colspan="3">2 GB or more</td><td>512 MB or more</td></tr>
<tr><td>Display</td><td colspan="4">XGA (1024 × 768 dots) or more</td></tr>
<tr><td>Hard disk capacity</td><td colspan="4">1 GB or more space is required during operation.</td></tr>
<tr><td>USB port</td><td colspan="4">At least one USB1.1 / USB2.0 port</td></tr>
<tr><td>Disk drive</td><td colspan="4">CD-ROM drive
(For setup CD installation)</td></tr>
<tr><td>Others</td><td colspan="4">• To use the analysis report setting function, install Microsoft® Excel. To execute Office update. Otherwise, operation becomes unstable.
• To use the HELP function, install Adobe Reader®.
• To apply the operational “NLDFT･GCMC” method, Corei3 or more processors.
• Install “Microsoft.NET Framework 2.0 or more”.</td></tr>
</table>

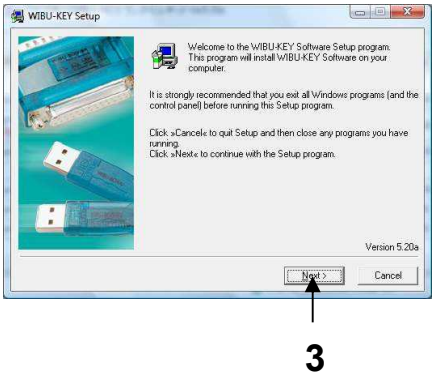
Chapter 2: Installation of the analysis program

This chapter describes the installation of the BELSORP analysis program on a personal computer. First, install the WIBU-KEY software. Then install the Analysis software.
(For instructions about the basic operating procedures for Windows, see the Windows instruction manual. The screen images may be different from those shown here, depending on your environment.)

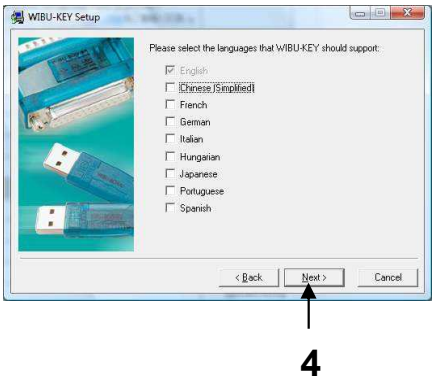
2-1. Installation of the WIBU-KEY program

* If the WIBU-KEY program is already installed,
First delete the WIBU-KEY program from your PC and then do the following.
(See section “3-2. Uninstalling the WIBU-KEY program” on page 16.)

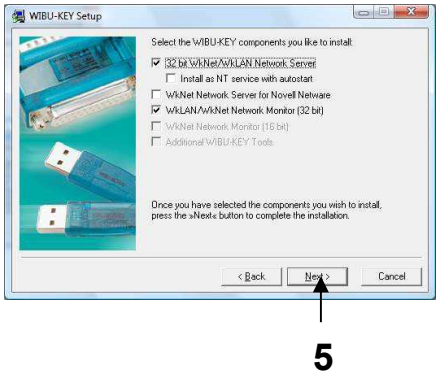
1. Put the Setup CD in the CD-ROM drive.
2. Run WkRt-Int.exe, which can be found in the WIBU-KEY device driver folder on the Setup CD. After reading this program for a moment, your PC displays the screen shown at right.
3. Click the [Next] button.



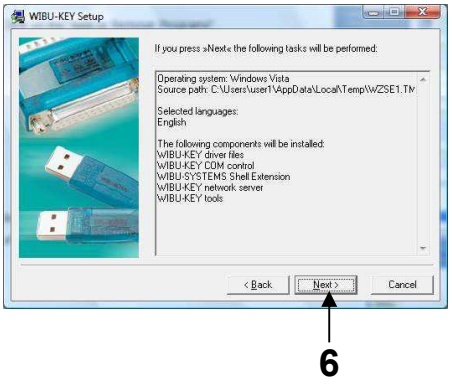
4. Choose “English” and then click the [Next] button.



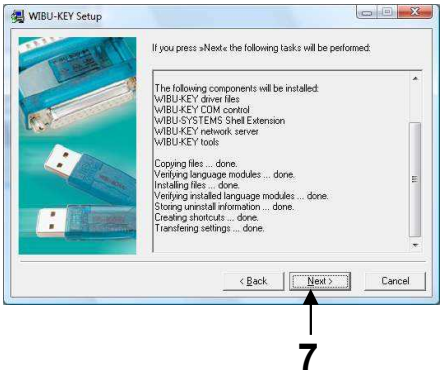
5. Click the [Next] button again.



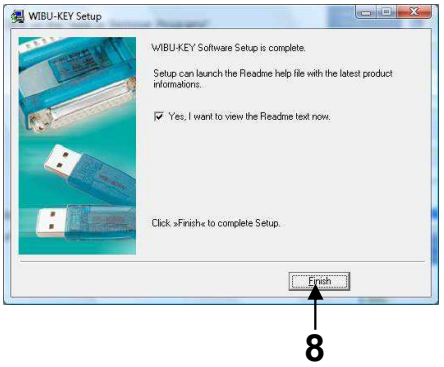
6. After clicking the [Next] button, your PC will start installing the WIBU-KEY driver.



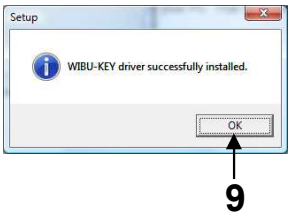
7. Click the [Next] button again.



8. Click the [Finish] button to end the installation.



9. When the window on the right appears, click the [OK] button.



10. Connect the WIBU-KEY for the BELSORP analysis program to a USB connector on your PC.
That completes the installation of the WIBU-KEY and driver.

2-2. Installation of the analysis program

* If the BELSORP program is already installed,
Delete the BELSORP program from your PC and then do the following.
(See “3-1. Uninstalling the analysis program” on page 15.)

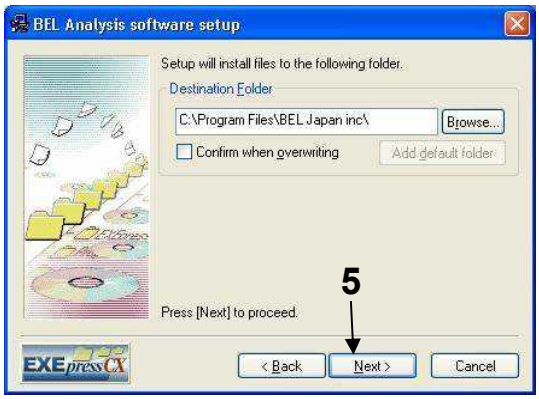
1. Put the Setup CD in the CD-ROM drive.

2. Run SETUP.EXE, which can be found in the Data analysis program folder on the Setup CD.

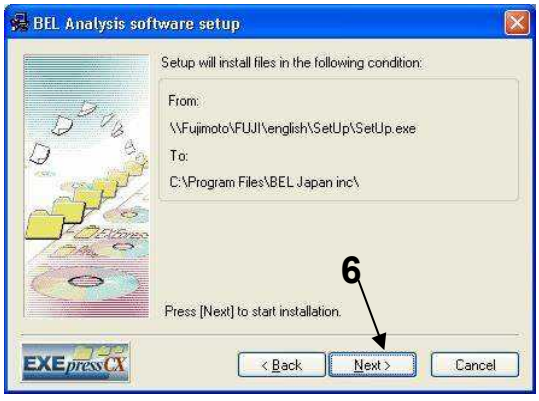
3. The installer will start and you will see window on the right.

4. Click the [Next] button.

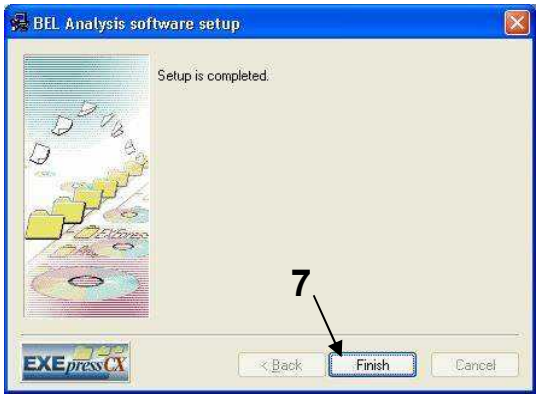
5. Confirm the installation destination folder and then click the [Next] button.



6. Click the [Next] button and the set up will start.



7. When the installation is complete, the screen on the right will appear. Click the [Finish] button.



2-3. File configuration of the analysis software

The file configuration right after the program is installed is as follows. Please note that, if some files are not in the specified folders, the analysis software may not operate normally.

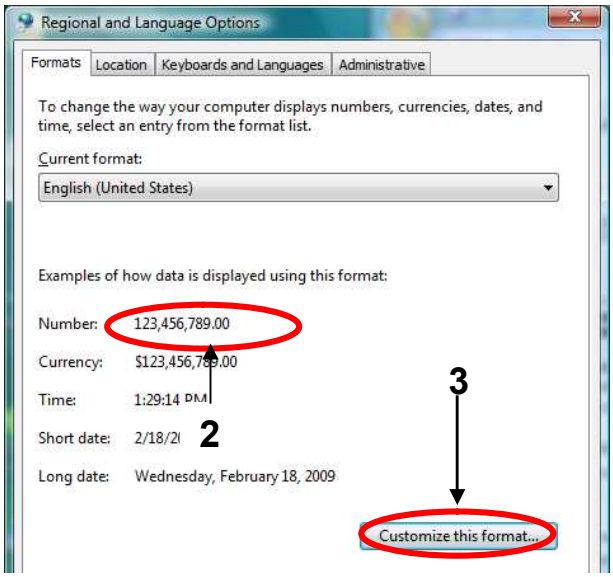
Folder configuration	Description	Details
BelAnalys	Installation folder	A different folder name can be used.
— BELMaster.exe	Execution file	
— *.dll	Expansion file used by the execution file	Be sure to place this file in the same folder as the execution file. Note: If you delete the expansion file, this software cannot normally operate.
— BELMaster_Doc.pdf	Help file	Be sure to place this file in the same folder as the execution file. If this file is deleted, or if the file name is changed, no information is displayed even if you click on [How to use this program] in the [Help] menu.
— ADSORPTIVE_INF.csv	Adsorptive data file	Be sure to place this file in the same folder as the execution file. If this file is not provided, the system automatically creates a file.
— DefFmt.xls	Report output format file	Be sure to place this file in the same folder as the execution file. If this file not is provided, the analysis report output function is disabled.
— T-DATA	T-DATA folder	Be sure to place this holder in the same folder as the execution file. If this folder is not provided, or if the folder name is changed, an error occurs with the T-interpolation user settings for the *t* method, αs method, DH method, BJH method, CI method, INNES method and MP method, and the HK method and SF method, and the analysis software cannot normally operate.
— *.t	Reference t-curve data	A different folder is also acceptable.
— *.as	Reference αs data	A different folder is also acceptable.
— *.HKS	HK method parameter	Indispensable for the HK method. Be sure to place this file in the T-DATA folder.
— *.SFS	SF method parameter	Indispensable for the SF method. Be sure to place this file in the T-DATA folder.
— *.TTI	T-interpolation user data	If this file is not provided, the system automatically creates a file.

2-4. Specifying a decimal point symbol and a date format

If the decimal point is specified as comma "," in the Windows settings, the analysis software will not operate normally. You can check this setting with the following procedure.

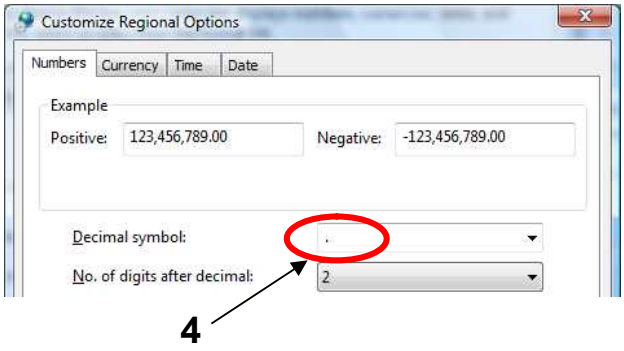
Specifying a decimal point

1. In the "Control Panel", select "Regional and Language Options".



2. Look at the "Samples" section and make sure the numbers show a period "." for a decimal point.

3. If a comma "," is selected as the decimal symbol, click the [Customize…] button. The "Customize Regional Options" window will open.

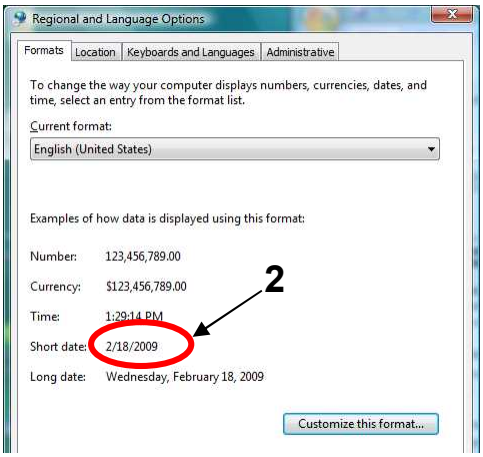


4. Select the "Numbers" tab and change the decimal point symbol to a period ".".

5. Click the [OK] button to store your changes and exit from these settings.

Specifying a date format

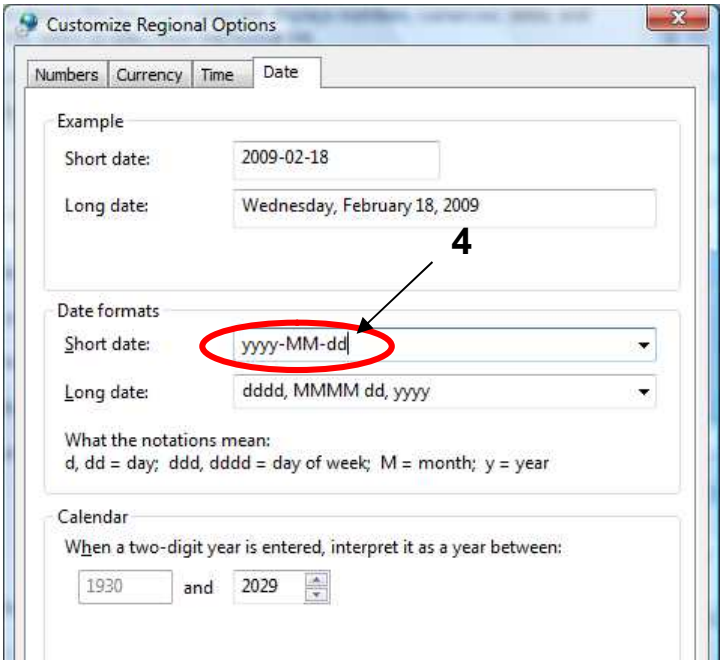
1. In the "Control Panel", select "Regional and Language Options".



2. Look at the "Samples" section and make sure the "Short date".

3. If the "yyyy/MM/dd" format is not selected, click the customized botton. The "Customize Regional Options" window will open.

4. Select the “Date” tab. Change the “Short date format” to “yyyy/MM/dd” and “Date separator” to “/”.
5. Click the [OK] button to store your changes and exit from these settings.



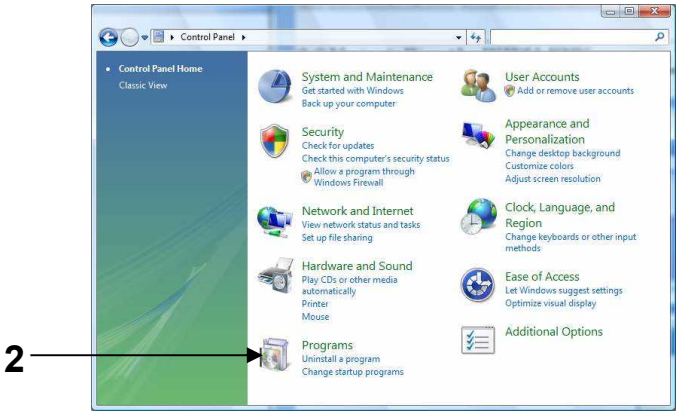
Chapter 3: Uninstalling the analysis program

This chapter describes the steps to uninstall the BELSORP analysis program. First, uninstall the analysis software. After that un-install the WIBU- KEY software.

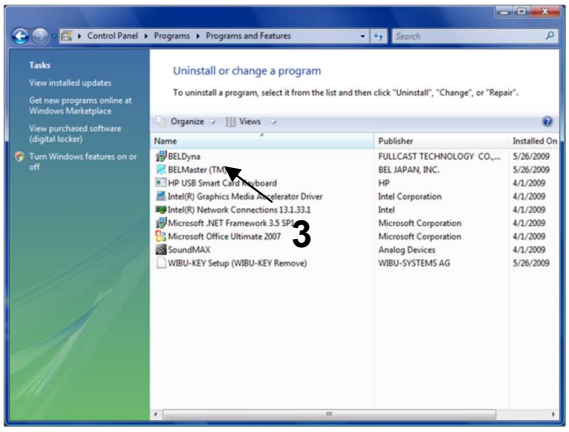
3-1. Uninstalling the analysis program

1. Open the Windows “Control Panel”.

2. Click on the “Uninstall a program”.



3. Select the “BEL analysis program” from the list of programs shown and click on the [Uninstall/Change] button.



4. Click the [Yes] button in the “EXEpress Uninstaller” window.

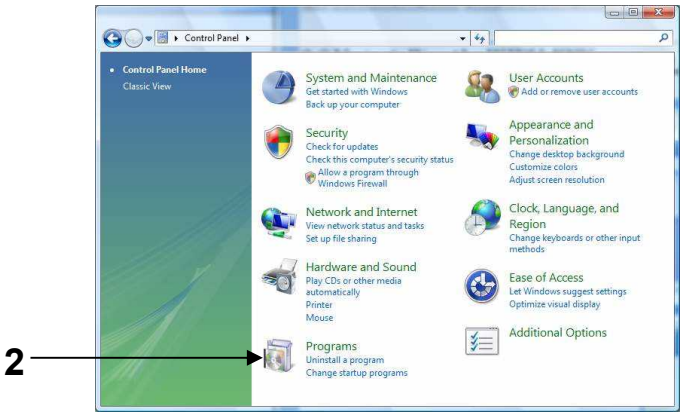
5. Then, your computer may ask you whether or not you really want to delete the shared files. If you are sure there will not be any problem in deleting them, click the [Delete] button. If you are not sure, click the [Save] button. If you are sure you want to delete all the files, click the [Delete all] button. If you want to leave all of them, click the [Save all] button.

6. If your computer displays the message “Unable to delete the file” during the uninstall process, click the [Yes] button and go ahead. When the uninstall window closes, the data analysis program has been uninstalled.

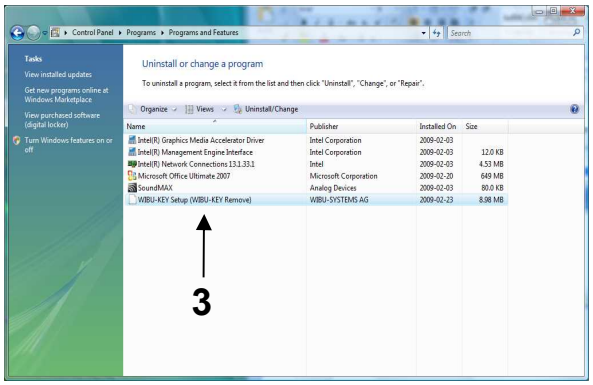
3-2. Uninstalling the WIBU-KEY program

1. Open the Windows “Control Panel”.

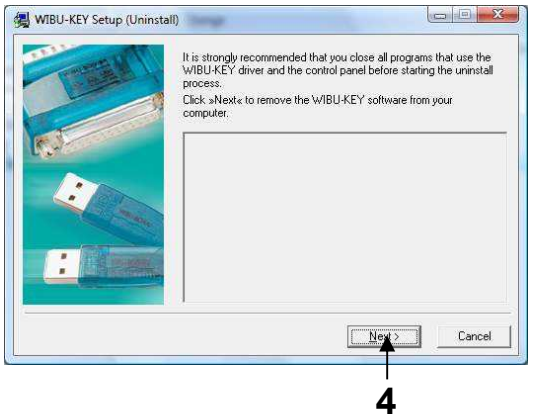
2. Click on the “Uninstall a program”.



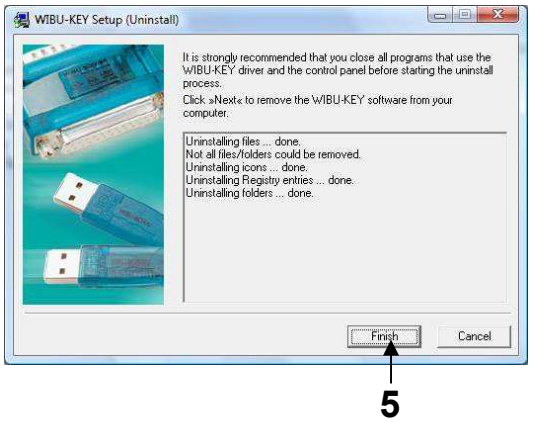
3. Select the “WIBU-KEY Setup (WIBU-KEY Remove)” from the list of programs and click on the [Uninstall/Change] button.



4. Follow the instructions in the WIBU-KEY Setup (WIBU-KEY Remove) window and click the [Next] button.



5. Click the [Finish] button to end the uninstall process of the WIBU-KEY program.



Basic Operation

Chapter 4: Starting and ending the program

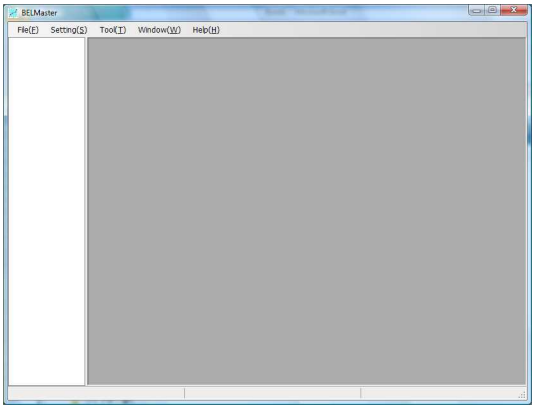
This chapter describes how to start and end the BEL analysis program.
(For details about basic Windows operations, see the Windows instruction manual. Depending on your system's environment, the screen images on your PC may be different from the images shown in this manual.)

4-1. Start up

1. Turn on your computer and start Windows.

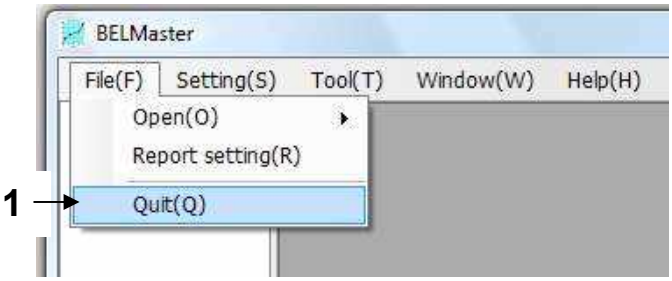
2. From the "Start" bar select "All Programs", "BELSORP" and "Data analysis program" in that order.

3. The BEL analysis program will start and the main window, shown on the right, will appear.

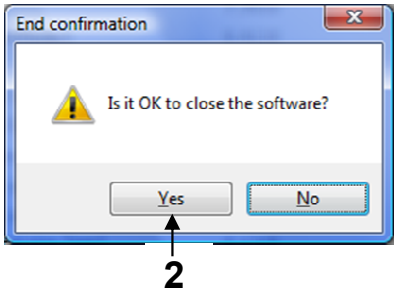


4-2. Quit

1. Select "File (F)" and then "Quit (Q)" from the BEL menu, That will end the BEL analysis program.



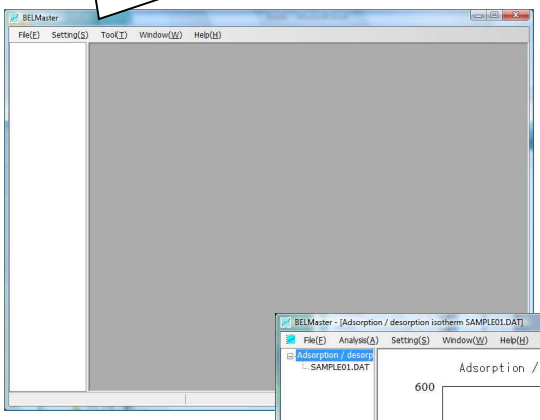
2. After the dialog box appears as shown on the right, select "Yes (Y)".



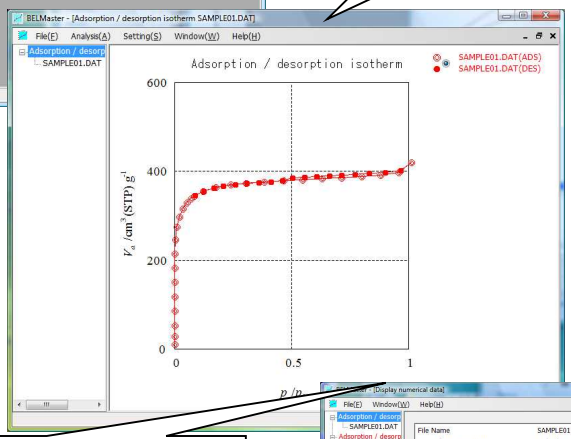
Chapter 5: “Main” window

Depending on the analysis conditions, one of three menus will be displayed in the “Main” window. This chapter briefly describes the contents of these menus and the function of the items in the menus.

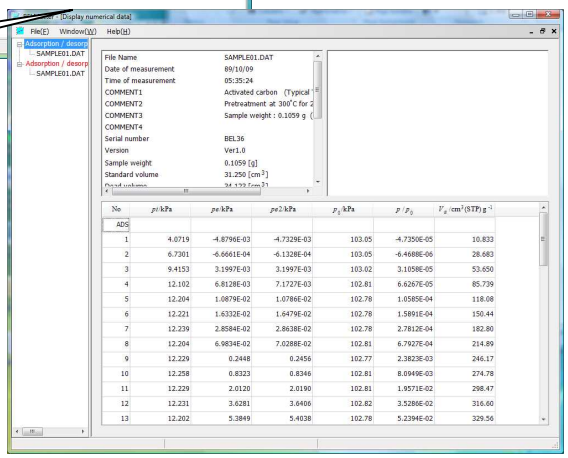
5-1. Initial menu
(The first menu displayed after starting the BEL analysis program)



5-2. Menu while analyzing data
(When the data is being displayed as a graph)

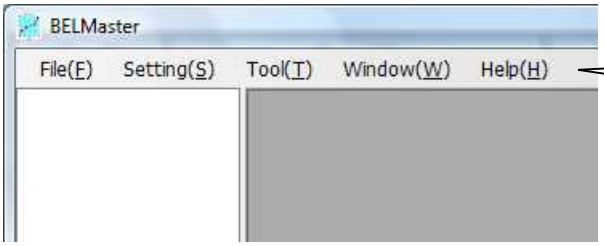


5-3. Menu while analyzing data
(When the data is being displayed as the numerical data)



5-1. Initial menu

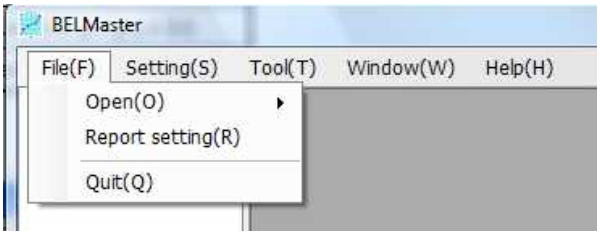
1) Menu contents



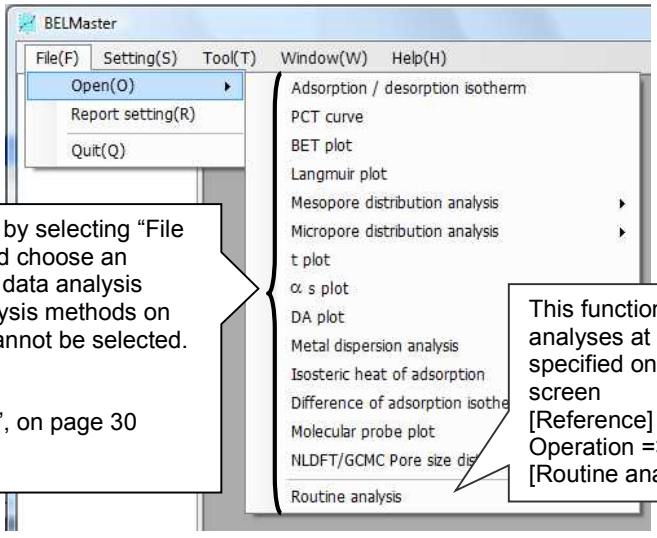
The first menu displayed after starting the BEL analysis program (no data file is open)

File (F)	Open (O)	Adsorption/desorpotion isotherm PCT curve BET plot : :
	Report settings (R)	
	Quit (Q)	
Settings (S)	Routine analysis setting (R) Adsorbent information (I)	
Tools (T)	Edit data (E)	
Help (H)	How to use this program (U)	
	Version info (V)	

2) "File (F)" menu



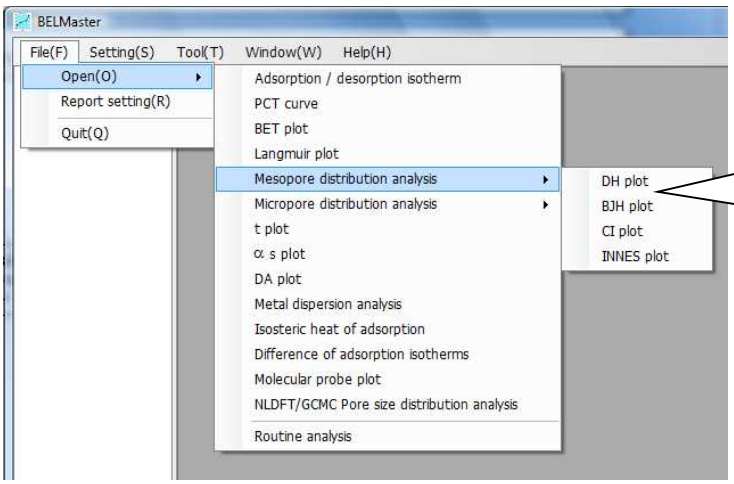
- "Open (O)" menu

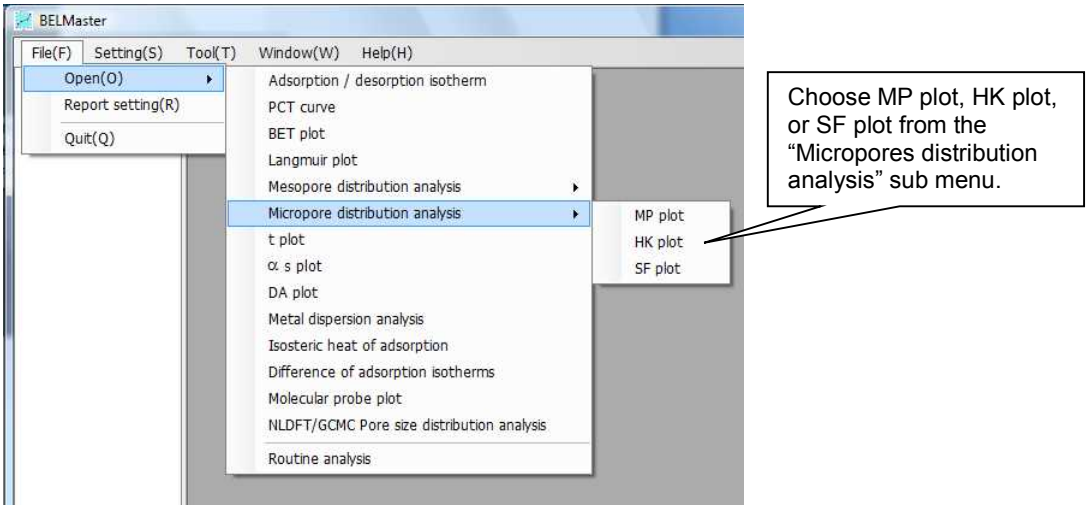


Open the data analysis window by selecting "File (F)". Then select "Open (O)" and choose an analysis method. The graphic data analysis screen will be displayed. Analysis methods on the menu that are grayed out cannot be selected.

[Reference]
Operation => "File open", on page 30
Analysis method => Page 62–

This function is used to execute multiple analyses at once. The analyses can be specified on the "Routine analysis setting" screen
[Reference]
Operation => Chapter 29
[Routine analysis] => Page 144





- "Report setting"

The analysis report setting screen will appear.

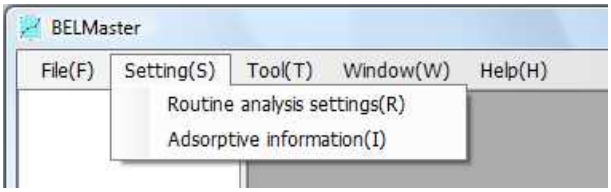
[Reference]
Operation => Chapter 31: Output an analysis report, on page 145.

Note: If Microsoft Excel is not installed on your PC, this function cannot be used.

- "Quit"

Select "File (F)" and then "Quit (Q) ". The analysis program will end.

3) "Settings (S)" menu



- Routine analysis settings (R)

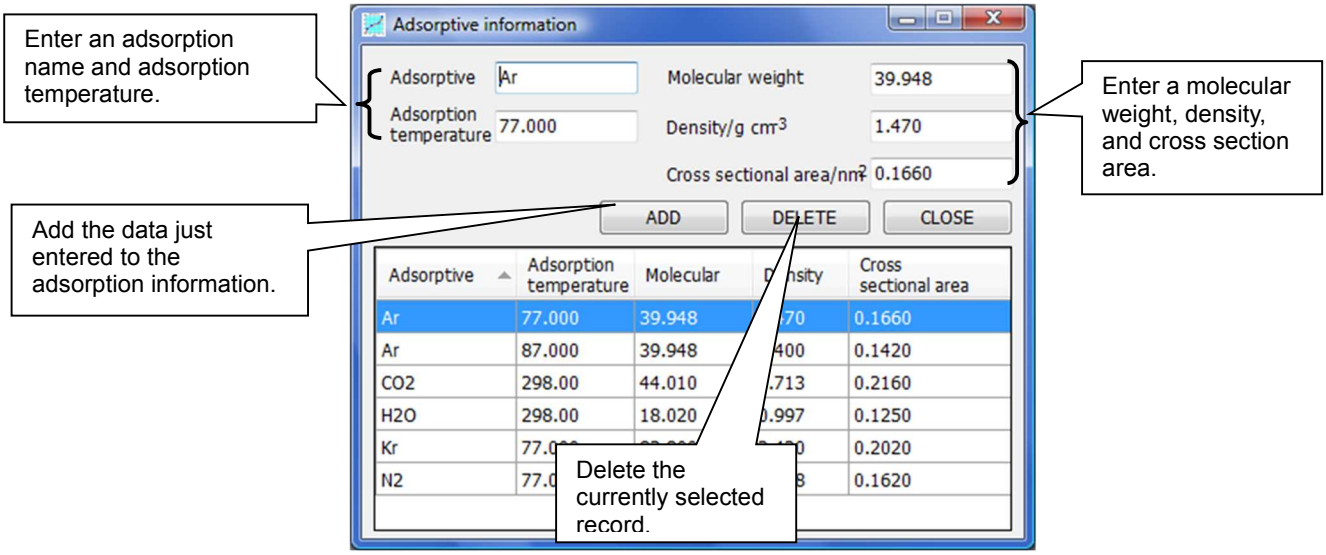
Specify the analysis methods to execute in a routine analysis.

[Reference]

Operation => Chapter 30: How to use [Routine analysis], on page 144.

- Adsorptive information

You can specify the adsorptive information (molecular weight, density, cross sectional area, etc.) to use in the analysis. If adsorptive information with an identical adsorption name and adsorption temperature is encountered while reading a measurement data file, the program will execute an analysis based on this adsorption information.



The default adsorptive information data is as follows.

Adsorptive name	Adsorption temperature / k	Molecular weight	Density / g cm^{-3}	Cross sectional area /nm^2
Ar	77.000	39.948	1.470[*1]	0.166[*4]
Ar	87.000	39.948	1.400[*1]	0.142[*2]
CO_2	298.00	44.010	0.713[*3]	0.216[*6]
H_2O	298.00	18.020	0.997[*4]	0.125[*6]
Kr	77.000	83.800	2.240[*5]	0.202[*6]
N_2	77.000	28.013	0.808[*1]	0.162[*6]

«Reference»

*1 ISO 15901-3

*2 ISO 18757

*3 National Institute of Standards and Technology, http://webbook.nist.gov/chemistry/fluid/

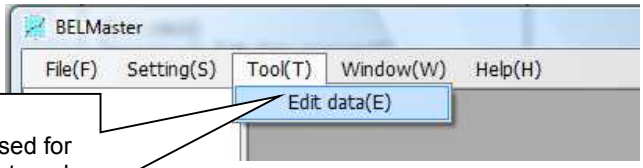
*4 Chemistry handbook basic 4th edition, Chemical Society of Japan, Maruzen Co., LTD.

*5 The properties of GASES & LIQUIDS, 4th edition, Robert C Reid, John M. Prausnitz, Bruce E. Poli

*6 Sicence of adsorption 2nd edition, Seiichi KONDOU, Tatuo ISHIKAWA, Ikuo ABE, Maruzen Co., LTD.

1) “Tools” menu

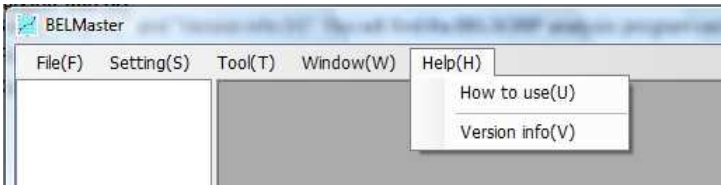
- “Edit data (E)”



Select “Tools (T)” and “Edit data (E)”.
Then you can edit the data settings used for the measurements (sample, adsorbent, and measurement conditions).

[Reference]
Operation => Edit data, on page 54.

2) “Help (H)” menu



- “How to use (U)”

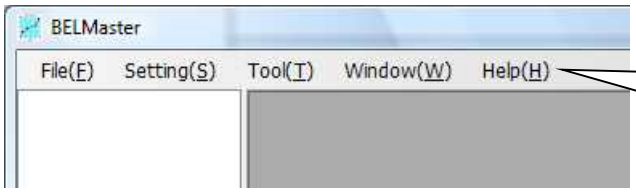
Select “Help (H)” and “How to use (U)”. The BELMaster manual can be refer here.
[Reference]
Operation => How to use the analysis program, on page 55.

- “Version info (V)”

Select “Help (H)” and “Version info (V)”. You will find the BELSORP analysis program version information here.
[Reference]
Operation => See BEL analysis program “Version information”, on page 55.

5-2. Data analysis menus (when the data window is a graph)

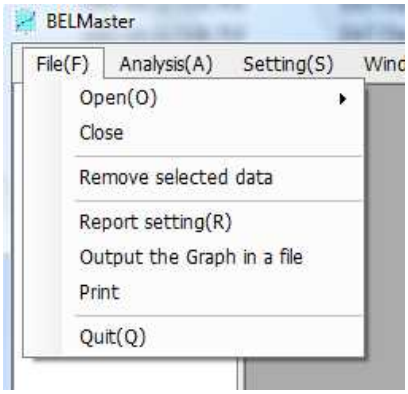
1) Menu structure



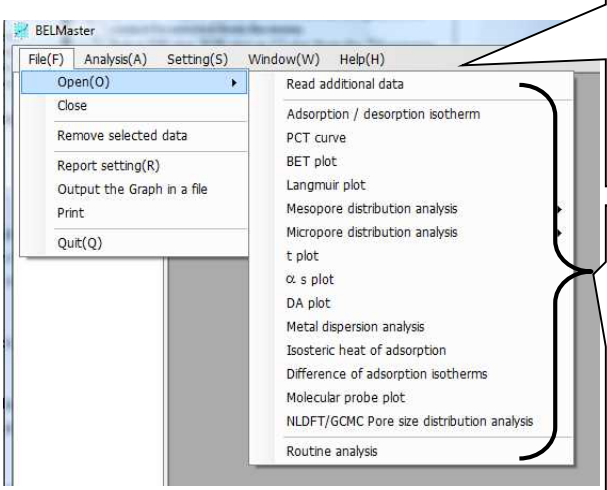
While analyzing data (more than one data set is open), this menu will appear when the active data analysis window is a graph.

File	Open (O)	Additional reading
		Adsorption/desorption isotherm PCT curve BET plot : :
	Close	
	Delete the selected data (Not displayed during the molecular probe analysis)	
	Report setting	
	Save as (Displays only the difference of adsorption isotherm analysis)	
	A printing result is output to a file	
	Print	
	Quit (Q)	
Analysis (Not displayed during the Molecular probe analysis)	Display numerical data	
	Adsorption/desorption isotherm PCT curve BET plot :	
Settings (S) Setting menu during Molecular probe analysis Analysis setting Edit data	Analysis parameters (A)	
	X-axis display settings (X)	
	Y-axis display settings (Y)	
	Plot settings (L)	
	Smoothing settings (S)	
	Routine analysis settings (R)	
	Adsorptive information (I)	
Window (W)	Cascade (C)	
	Tile horizontally (H)	
	Tile vertically (T)	
	1 Data name.dat 2 Data name.dat : (Names of currently open data files)	
Help (H)	How to use this program (U)	
	Version info (I)	

2) "File (F)" menu



- "Open (O)" menu



Select "File (F)," "Open (O)," and then "Read additional data". You can display a maximum of five sets of data overlaid on the currently active data analysis window.
[Reference]
Operation => Adding data file to active window (graph), on page 34

Select "File (F)," "Open (O)," and then either analysis method. You can display a different data analysis (graph) in a new window. Analysis methods that are grayed out cannot be selected from the menu.
Select DH plot, BJH plot or CI plot from the "Mesopores distribution analysis" sub window.
Select MP plot, HK plot, or SF plot, from the "Micropores distribution analysis" sub menu.
[Reference]
Operation => "File Open", on page 30.
Analysis method => Page 62-

- "Save as"

This function is only available when "Difference of adsorption isotherms" analysis is selected. Save the "difference of adsorption isotherms" data, shown in the currently active data analysis window, in an adsorption isotherm file. The saved data can be analyzed using other analysis methods such as a Langmuir plot.

- "Close"

Select "File (F)" and "Close". This will close the currently active data analysis window (graph).

- "Delete selected data"

Select "File (F)" and "Delete selected data". The program will delete the selected data (data whose check box has been selected) in the currently active data analysis window.

- "Report setting"

An analysis report setting screen will appear.
[Reference]
Operation => Chapter 31: Output an analysis report, on page 145.
Note: If Microsoft Excel is not installed on your PC, this function cannot be used.

- "A printting result is output to a file "

Select "File (F)" and "A printting result is output to a file". You can save the results in a file. The graph of the active analysis window of the currently active data analysis window can be saved in bitmap or meta file format.
[Reference]
Operation => 9-1. Saving a data analysis, on page 48.

- "Print"

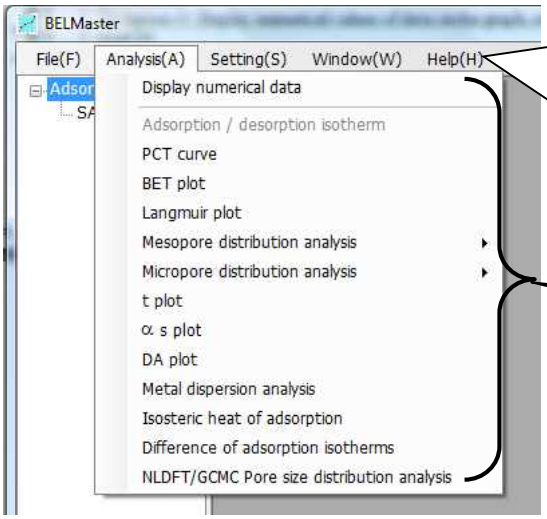
Select "File (F)" and "Print". Then you can print a data analysis graph of the active analysis window.
[Reference]
Operation => Print data analysis (graph), on page 51

- "Quit"

Select "File (F)" and then "Quit (Q)" to end the BEL analysis program.

3) "Analysis (A)" menu

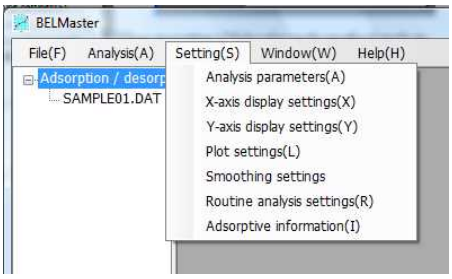
The "Analysis (A)" menu is not displayed if the Molecular probe method analysis window is active.

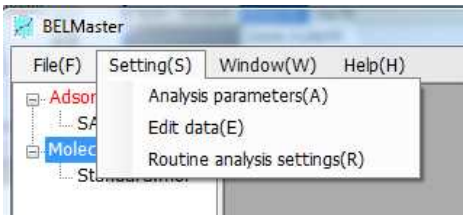


If you select "Analysis (A)" and then "Display numerical data", the program will open a new data analysis window and show you the numerical data. It will display numerical data for the active data (data whose check box has been selected) in the currently active window.
[Reference]
Operation => Display numerical values of data on the graph, on page 35.

If you select "Analysis (A)" and then any analysis method, the program will open a new data analysis window and display the data for analysis. It displays data analysis for the active data (data whose check box has been selected) in the currently active window.
Select DH plot, BJH plot, or CI plot, INNES plot from the "Mesopores distribution analysis" sub window. Select MP plot, HK plot, or SF plot, from the "Micro pores distribution analysis" sub menu.
[Reference]
Operation => "File open", on page 29.
Analysis method => Page 62–

4) "Settings (S)" menu



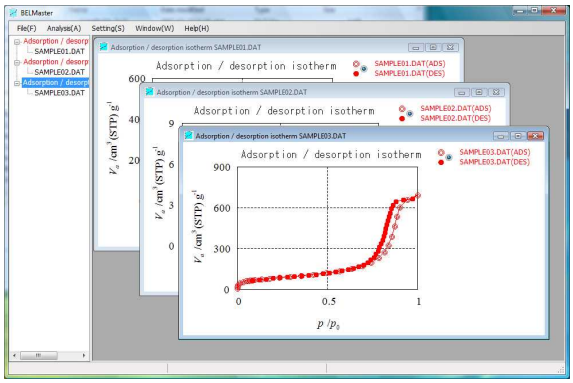


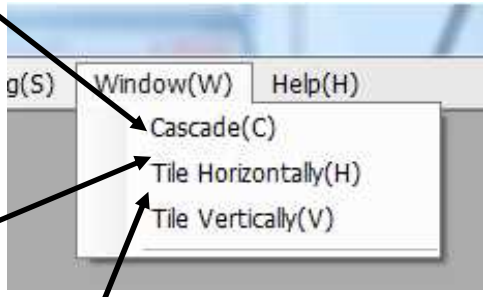
When executing a Molecular probe method analysis.

Select "Setting(S)" and then any of the items you want to set. A setting window will open and you can specify individual settings.
[Reference]
Operation => Chapter 7 "Setting" window, on page 37

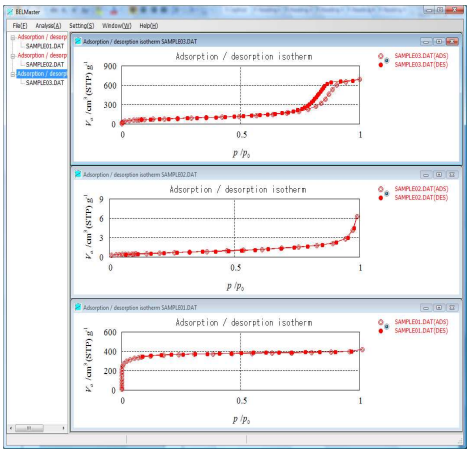
5) "Window (W)" menu

Select "Window (W) " and then "Cascade (C)".
Multiple windows are displayed by overlapping them.

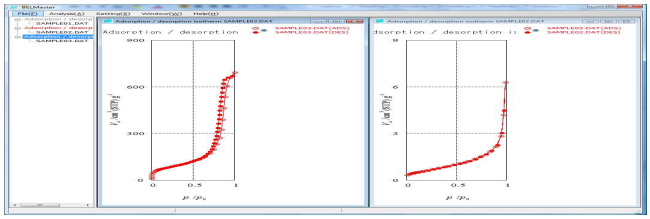




Select "Window (W)" and then "Tile Horizontally (H)". The program will display the windows arranged horizontally.



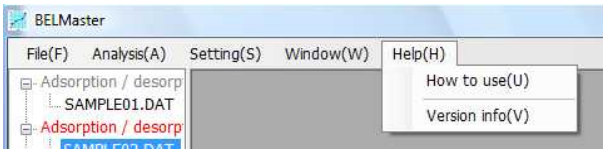
Select "Window (W)" and then "Tile Vertically (T)".
The program will display the windows arranged vertically.



6) "Help (H)" menu

- "How to use this program (U)"

Select "Help (H)" and "How to use (U)". Then you can read the BELMaster manual.



[Reference]

Operation => How to use BEL analysis program, on page 54.

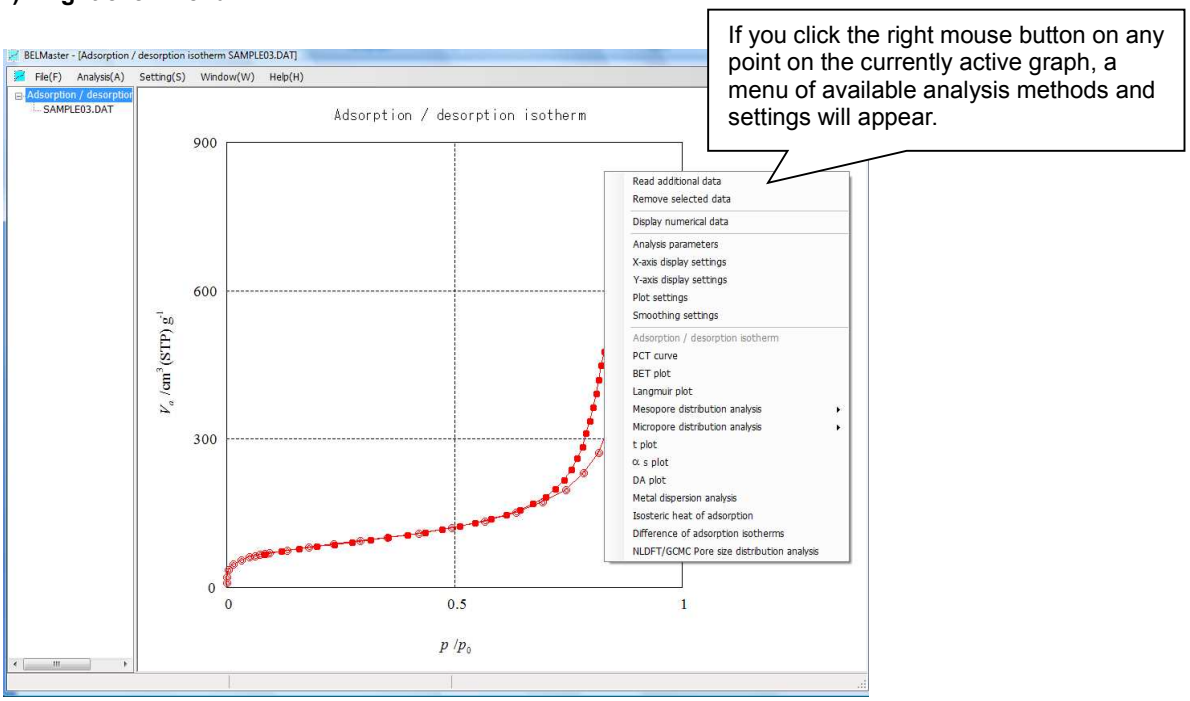
- "Version info (V)"

Select "Help (H)" and "Version info (V)". You will see version information about the BELSORP analysis program.

[Reference]

Operation => "Version information" about the BEL analysis program, on page 54.

7) Right click menu



- "Version info (V)"

Select "Help (H)" and "Version info (V)". You will see version information about the BELSORP analysis program.

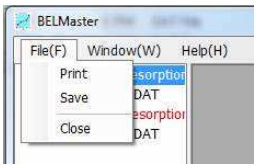
[Reference]

Operation => "Version information" about the BEL analysis program, on page 54.

7) Right click menu

5-3. Menus during data analysis (when the active data is numeric)

1) "File (F)" menu



- "Print"

Select "File (F)" and then "Print". You can print the numerical data from the active analysis window.

[Reference]
Operation => Print the data analysis (of numerical data), on page 51.

- "Save"

Select "File (F)" and then "Save". You can save the numerical data from the currently active data analysis window.

[Reference]
Operation => Save data analysis (numerical data), on page 48.

- "Close"

Select "File (F)" and "Close". The currently active data analysis window (numerical data) will close.

Chapter 6: Reading in analysis data

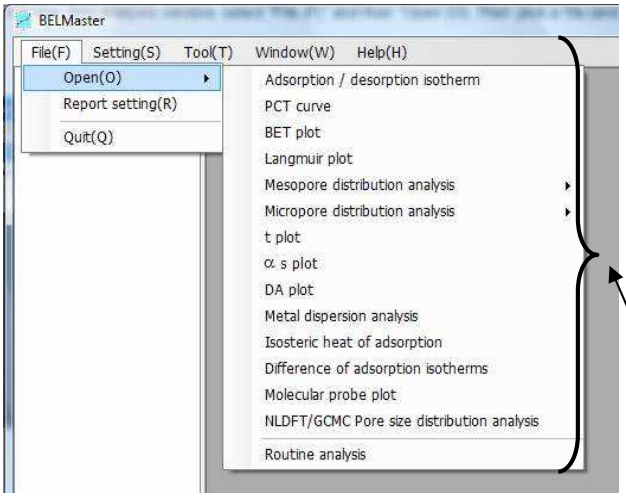
This chapter describes how to read in data that were measured by BELSORP series apparatuses, and how to display the graphis and numerical.

6-1. “File open”

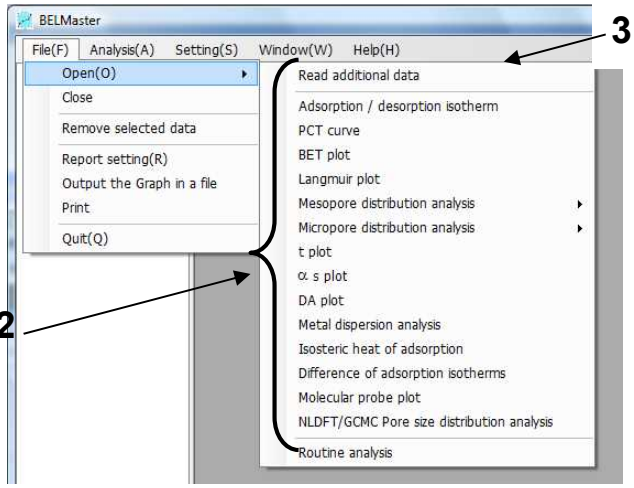
1. The following methods can be used to select a data analysis file.
   Reading data into a new data analysis window
   - Select from the analysis program menu 2

   Read additional data into the active data analysis window.
   - Select Additional Data from the analysis program menu 3
   - Select Additional Data from the menu displayed by right clicking the mouse on a graph 4

2. To open a file in a new data analysis window, select “File (F)” and then “Open (O). Then pick a file (and an analysis method).



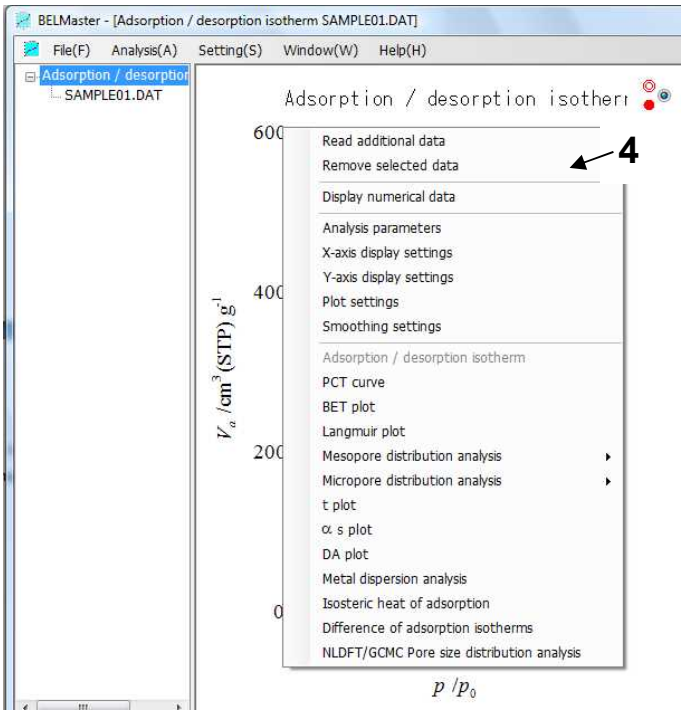
Initial menu



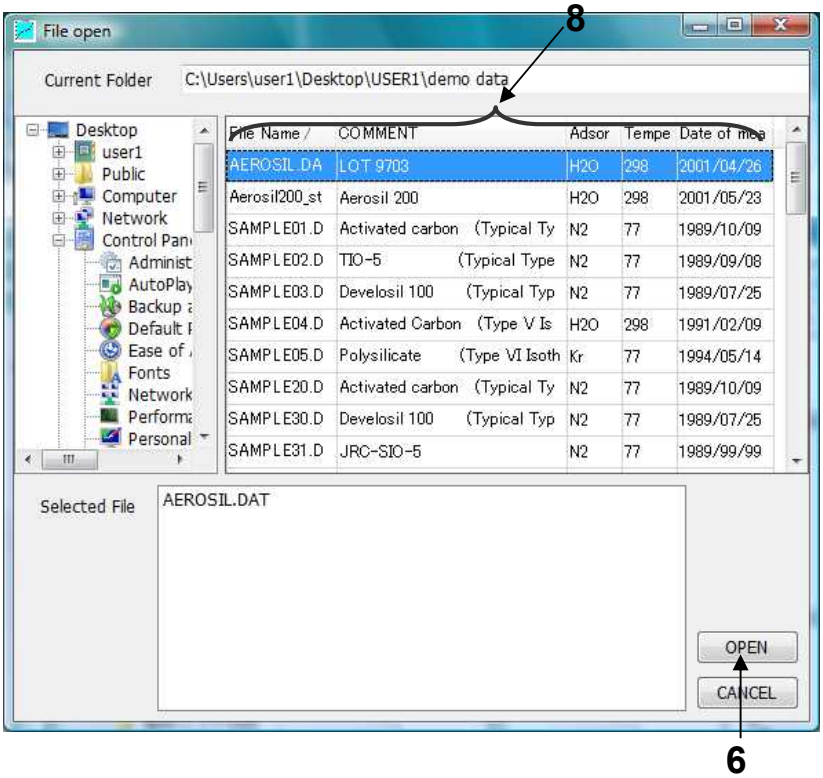
Menu while analyzing data

3. To add data to the active data analysis window, select “File (F)”, “Open (O)” and then “Read additional data”.

4. Move the cursor on the graph and click the right mouse button. Select “Read additional data” from the menu that pops up to add data to the active data analysis window.

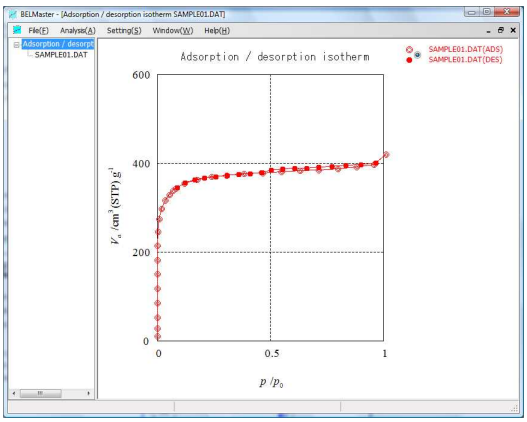


5. After step 2, 3 or 4, the “File open” window shown below will appear.



6. Select the data file you want to analyze, and click the [OPEN] button. The program will read in the specified file. Open multiple data files by holding down the [Ctrl] key and clicking on the various files you want.

7. The program will analyze the data using the specifie d analysis method and display a data analysis graph. The figure on the right is an example of an adsor -ption/desorption isotherm.

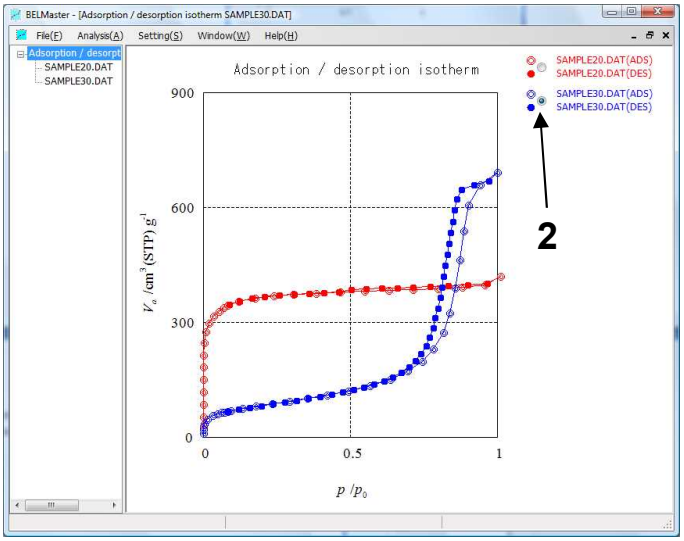


8. To change the order in which data is listed, click on the name of an item on the top line, such as “File name” or “comment name”. The program will sort the list according to the selected item. An up arrow “△“ on the left of the item name means that the data are displayed in ascending order. A down arrow “▽“ on the left means that the data are displayed in descending order.

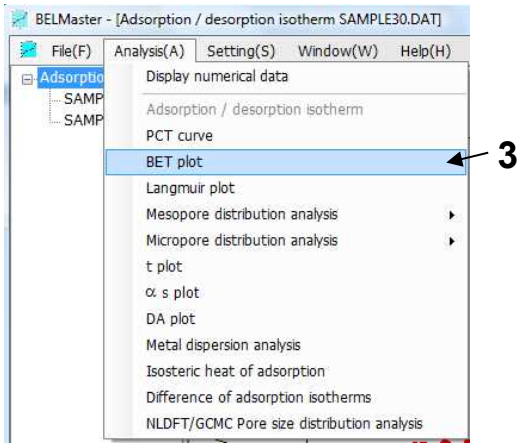
6-2. Analysis of active data (graph)

1. Two procedures can be used to analyze the currently graphed data using another analysis method.
   - Select from the BEL analysis program menu 3
   - Click the right mouse button on the graph and select from the menu that pops up 4

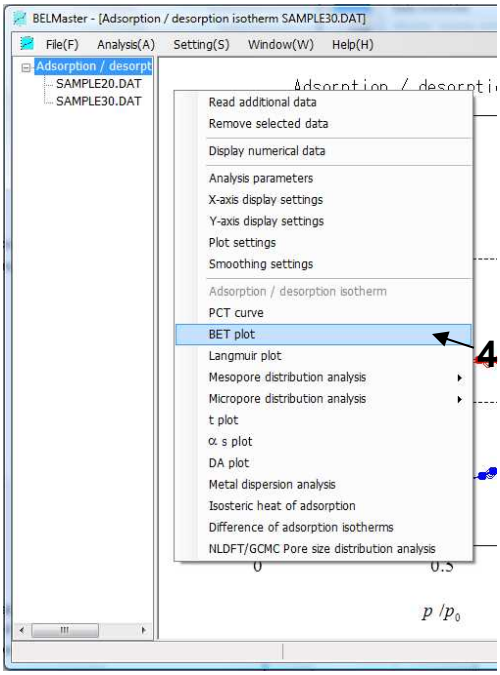
2. Select the data you want to analyze. If more than two data curves are drawn in a window, check the box for data you want to analyze.



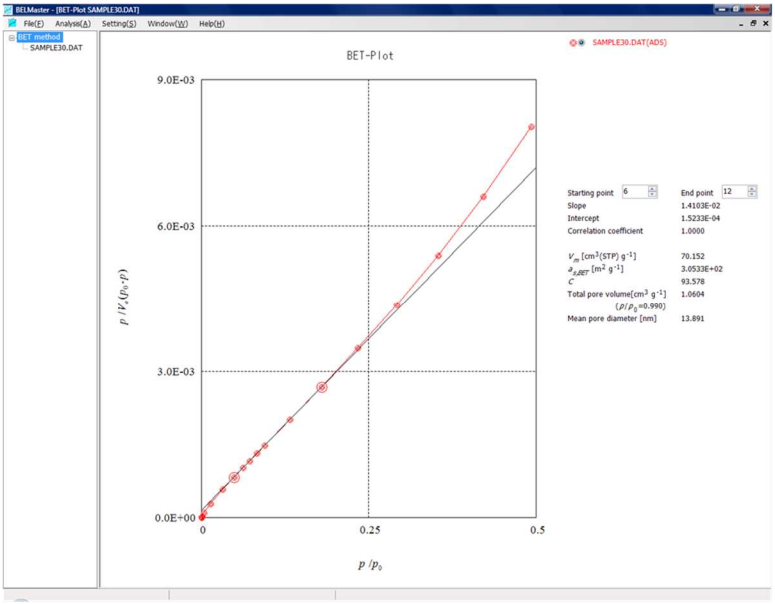
3. Select “Analysis (A)” and then an analysis method from the “Analysis” method menu.



4. Move the cursor onto the graph and click the right mouse button. The analysis methods menu will appear. Select a method from this menu.



4. A new data analysis window will be opened, and a graph of the specified analysis will be displayed.
The figure on the right is an example of a “BET plot”.



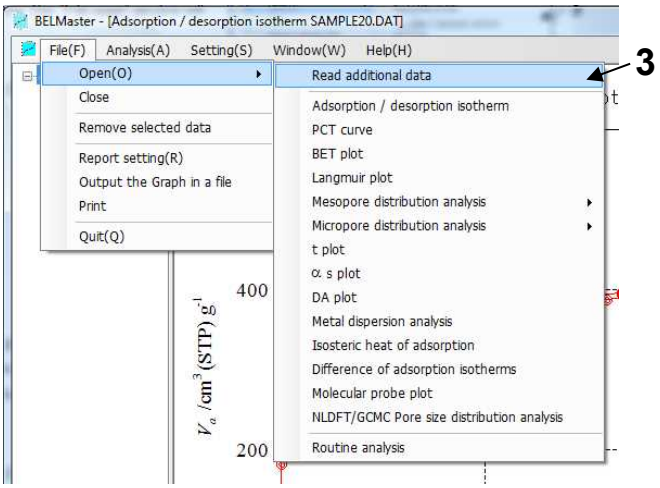
6-3. Adding data files to the active window (graph)

1. You can add another data analysis curve to the current analysis graph window. The curves will be overlapped.
   The following three methods can be used for reading in additional data.
   - Select from the BEL analysis program menu 3
   - Click the right mouse button on the graph and select from the menu that pops up 4
   - Drag and drop ..... 5 to 8

   The maximum number of data sets that can be read in one window is as follows.
   - Difference of adsorption isotherms and an iisosteric heat of adsorption:..... Two data set per window
   - Molecular probe method..... One data sets per window
   - Adsorption/desorption isotherm and analysis methods other than those above: ..... Five data set per window

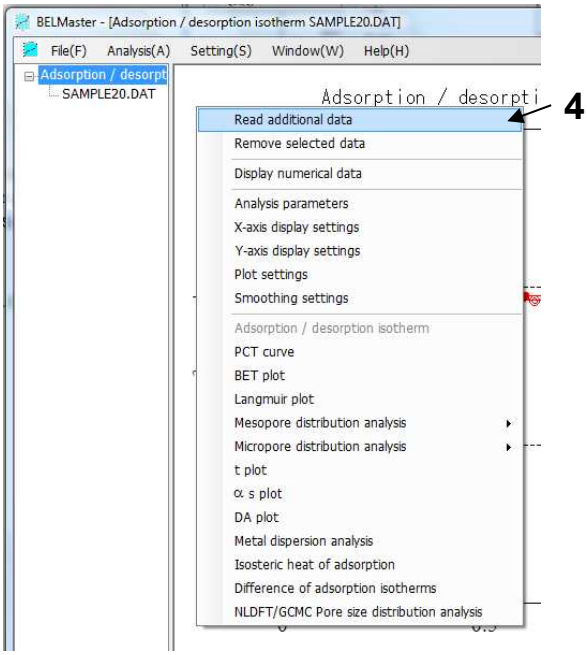
2. Click on the data analysis window you want to add to, to make it active.

3. Select “File (F),” “Open (O)” and then “Read additional data” on the analysis program menu. The “File open” window will appear. Select a file.
   [Reference]
   How to select a file => “File open”, on page 30.



4. Or, move the cursor on the graph and click the right mouse button. You can select “Read additional data” from the pop-up menu. The “File open” window will appear. Select the data file from it.

   [Reference]
   How to select a file => “File open”, on page 30.

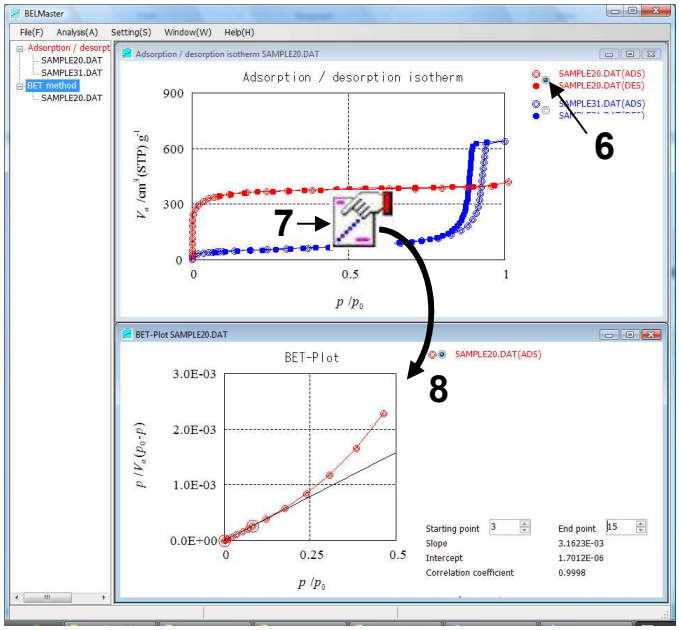


5. You can add data from another data analysis window to the current graph by dragging and dropping.

6. Select the data you want to add to another analysis graph.

7. Click the left mouse button on the graph. The icon will change to “ ”. This means that dragging and dropping is possible with the selected graph.

8. Keep the left mouse button pressed and move the mouse to the graph you want to add to. Then, release the left mouse button.

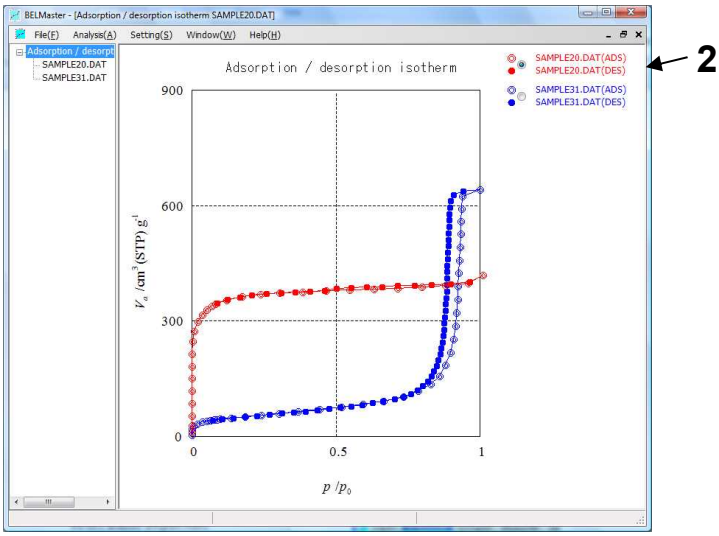


9. After analyzing data using a specified analysis method, the program displays this data overlapped on the graph.

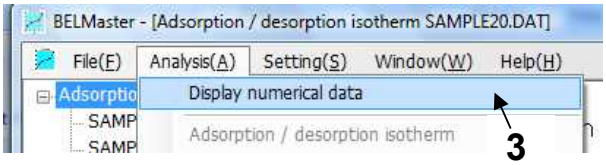
6-4. Display the numerical values of data on the graph

1. Two procedures can be used to display the numerical values of data on the current graph.
   - Select the data set from the BEL analysis program menu 3
   - Select the data from the menu that pops up when you click the right mouse button 4

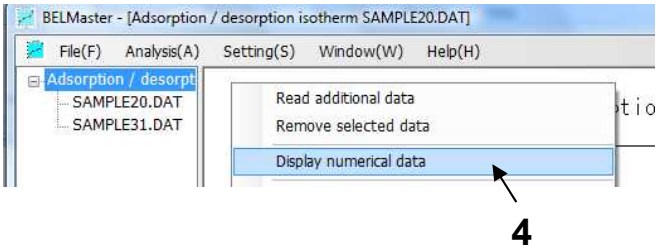
2. Select the data set you want to display as numbers. If more than two data sets are drawn on a window, check the box for the data you want to display.



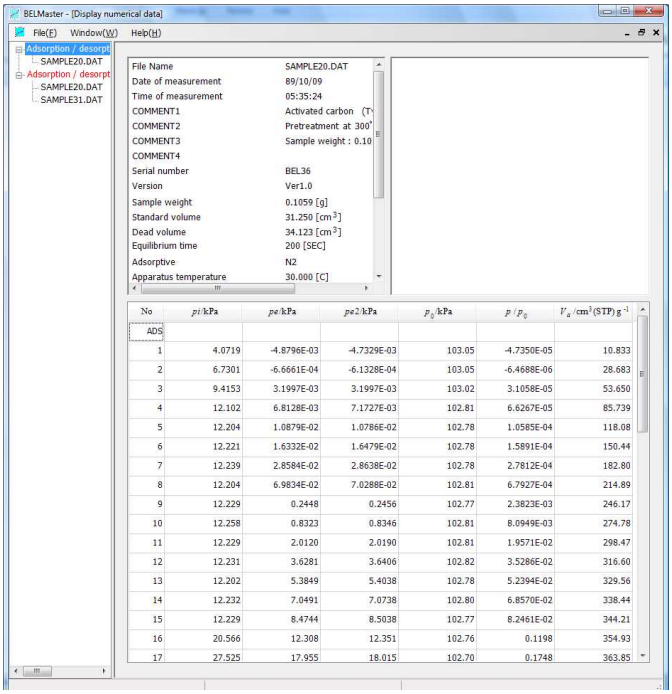
3. Select “Analysis (A)” and then “Display numerical data” from the BEL analysis program menu.



4. Move the cursor on the graph and click the right mouse button. Select “Display numerical data” from the pop-up menu.



5. A new data analysis window will open and display the numerical data from the specified data analysis.



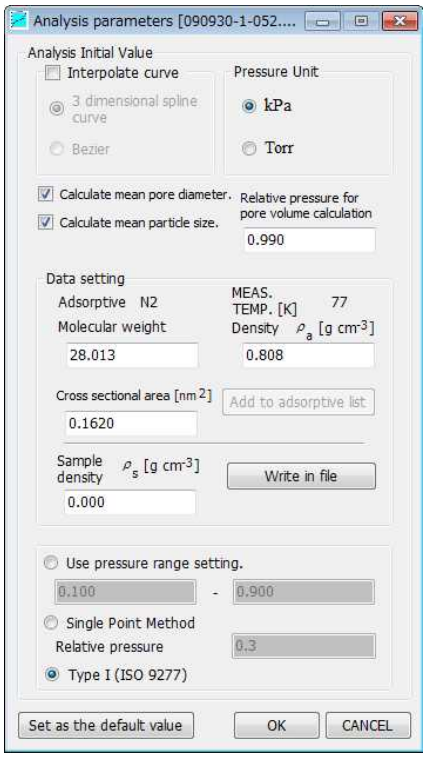
Chapter 7: “Setting” window

This chapter describes various parameter settings used for the analysis, graphic display and printing. Two methods can be used to display the “Settings” window.
- Select “Settings” from the measurement software menu.
- Put the cursor on the graph, right click and select the “Settings” from the popup menu.

When through setting the items, click the [OK] button and the settings will become effective. If you click [Set as the default value], the current settings will be stored as the default settings. Default settings are created for each type of analysis.

7-1. Analysis parameters

Specify the various parameters used for the calculations performed by each analysis in the “Analysis parameters” window. Below we describe how to set “Interpolate curve,” “Pressure unit,” and the “Data setting”. For details, see the operation description form each analysis type.



Analysis setting window for the BET plot.

1) Settings to “Interpolate curve”

Three methods can be used to draw an interpolated curve on a graph: “Linear,” “3 dimensional spline curve” and “Bezier curve”.

Linear ·····Click off “Interpolate curve”.
3 dimensional spline curve ·····Click on “Interpolate curve,” and then click on “3dimensional spline curve”.
Bezier curve ·····Click the “Interpolate curve,” and then click the “Bezier curve”.

2) Pressure unit for numeric data

The “pressure unit” selection section will be seen on the analysis setting screen for analyses other than the “adsorption/desorption isotherm” analysis.

This setting allows you to choose “kPa” or “Torr” as the pressure unit when displaying numerical data.

Note: In the “adsorption/desorption isotherm” analysis, you can choose the pressure unit to use for numerical data on the “X axis display settings” window.

3) Data setting

The density and adsorption molecular weight, as well as the sample molecular weight must be entered, depending on the analysis method. You can enter these parameters in this window.

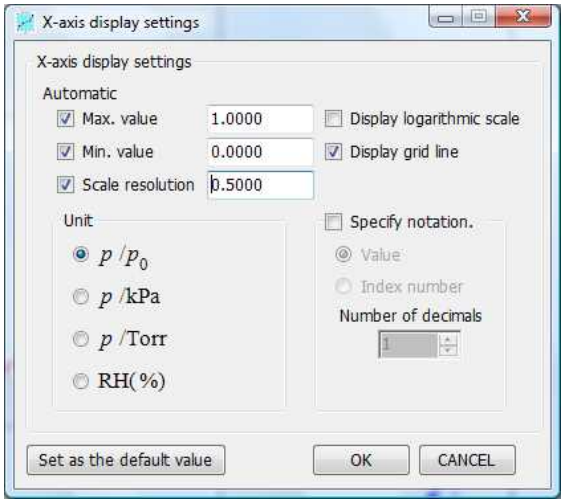
Adsorptive molecular weight	Enter the molecular weight of the adsorptive
Cross sectional area	Enter the Cross sectional area [nm^2]
Adsorptive density	Enter the density [g cm^{-3}] of the adsorptive
[Add to adsorptive list] button	If the adsorptive name does not exist and the adsorption temperature is not in the adsorptive information record, click this button. The adsorptive molecular weight, cross sectional area, and density that are currently entered can be added to the list. To change or delete adsorptive information that has already been recorded, select “Settings” and then “Adsorptive info.” [Reference] => “Setting” menu, on page 22.
Adsorbent molecular weight	Enter the molecular weight of the samples.
Sample density	Enter the density of the sample (g cm^{-3}).
Sample specific surface area	Enter the specific area of the sample (m^2 g^{-1}).
[Write in file] button	Save the sample molecular weight, sample density, and sample specific area currently entered in the measured data file.

7-2. X axis display settings

You can change the maximum value, minimum value, and scale resolution on the “X-axis display settings” window.

You can also change the units and notation.

Click on the [Set as the default values] button, and the currently set values will become the default for that analysis.



“X-axis display settings” window for adsorption isotherm.

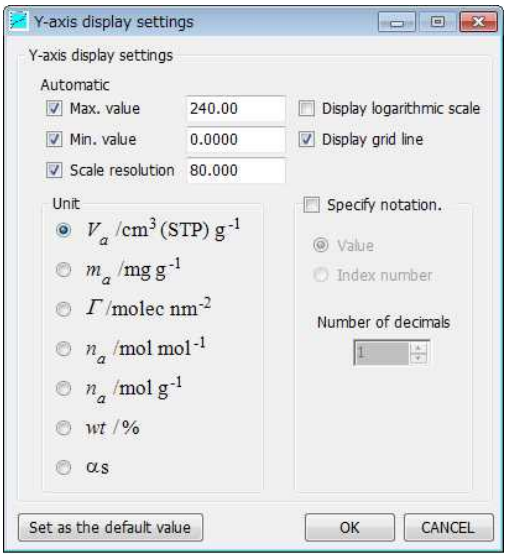
Automatic	Switch between auto/manual for the maximum and minimum values and the scale resolution of an axis.
Setting input box	When you want to enter the maximum, minimum, and scale resolution manually, change [Autmatic check box] by clicking off it. Then enter the values as numbers.
Unit	Select the units for the X axis. The units that can be selected vary with the analysis type.
Display logarithmic scale	Select whether or not to display a logarithmic scale. When this is selected, you cannot enter 0 as the maximum or minimum values.
Display grid line	Select whether or not to display grid lines on the graph.
Specify notation	By clicking this check box, you can select the notation used for the scales. Choose between the numerical value and the exponent (If this box is not checked, the display will be set automatically.). Then number of digits below decimal can be entered here.

7-3. Y axis display settings

You can change the maximum value, the minimum value and the scale resolution on the “Y-axis display settings” window.

You can also change the units and notation.

Click on the [Set as the default values] button, and the currently set values will become the default for that analysis.



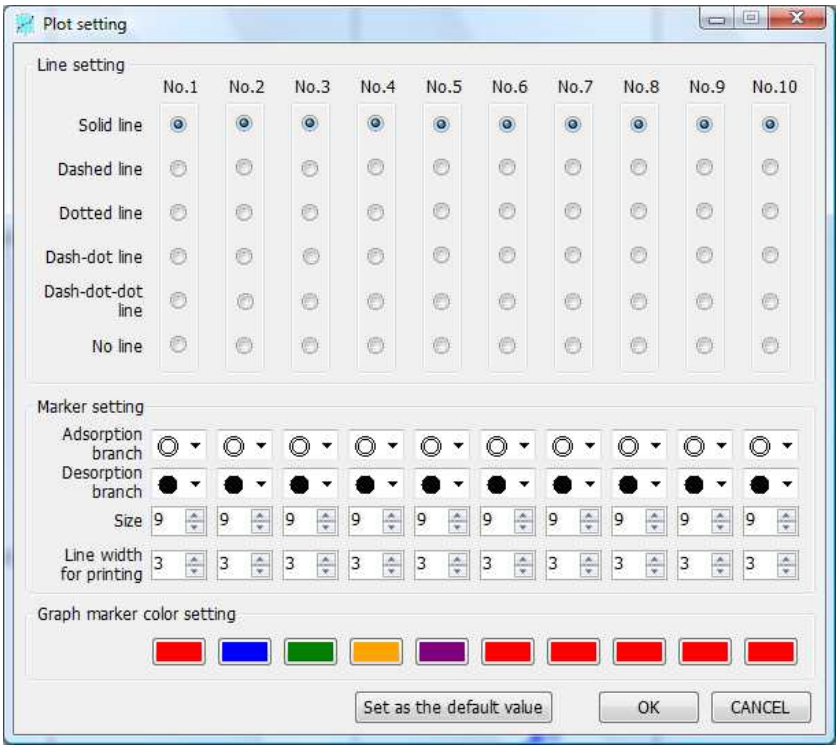
“Y-axis display settings” window for adsorption isotherm.

Automatic	Switch between auto/manual for the maximum and minimum values and the scale resolution of an axis.
Setting input box	When you want to enter the maximum, minimum, and scale resolution manually, change [Autmatic check box] by clicking off it. Then enter the values as numbers.
Unit	Select the units for the Y axis. The units that can be selected vary with the analysis type.
Display logarithmic scale	Select whether or not to display a logarithmic scale. When this is selected, you cannot enter 0 as the maximum or minimum values.
Display grid line	Select whether or not to display grid lines on the graph.
Specify notation	By clicking this check box, you can select the notation used for the scales. Choose between the numerical value and the exponent (If this box is not checked, the display will be set automatically.). Then number of digits below decimal can be entered here.

7-4. Plot settings

The line types and markers for graph display can be specified on the “Plot settings” screen.
Click the [Set as the default value] button to save the current settings as the default.

Note: You cannot specify the “Plot settings” with the “Molecular probe method”. However, you can do so in the “Analysis settings”.

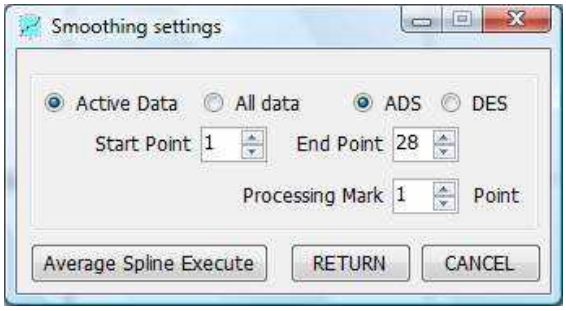


“Plot setting” window

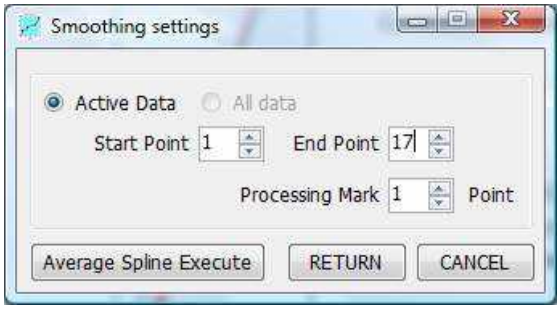
Line setting	Select the line type for data No. 1 to 10.
Line width for printing	Select the line thickness to use when printing.
Adsorption branch	Select the data point marker for the adsorption side.
Desorption branch	Select the data point marker for the desorption side.
Size (marker size)	Set the marker size.
Graphic marker color setting	Select the colors used for markers and lines.

7-5. Smoothing settings

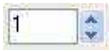
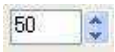
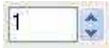
The selected data analysis results can be smoothed with these settings.



"Smoothing settings" window for the adsorption/desorption isotherm



"Smoothing settings" window for other analyses.

Active Data or All data	Select a data, "Active Data" or "All data", for the smoothing.
Active Data 	Select a branch for the smoothing process on the "adsorption/desorption" graph.
Starting Point 	Specify a smoothing starting point in the data.
End Point 	Specify a smoothing end point in the data.
Processing Mark  Point	Specify the number of processing points to smooth.
[Average Spline Execute] button	Smooth the data.
[RETURN] button	Return the data to their condition before smoothing.
[CANCEL] button	End the process and close the window.

Chapter 8: Data analysis window

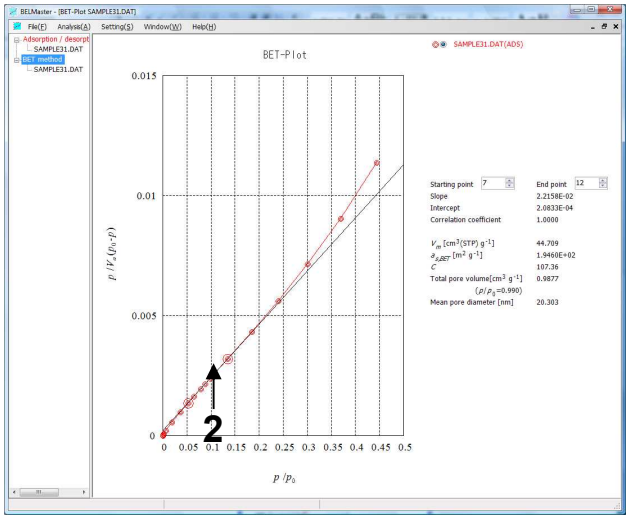
A “graphic” window and a “numerical value data” window are available to display the data analysis. This chapter describes the operations common to the “graphic” window. For details about operations specific to each analysis method, see Chapters 11 to 31.

8-1. Display plot data details

You can display coordinates of the plot data on a graph using the procedures below.

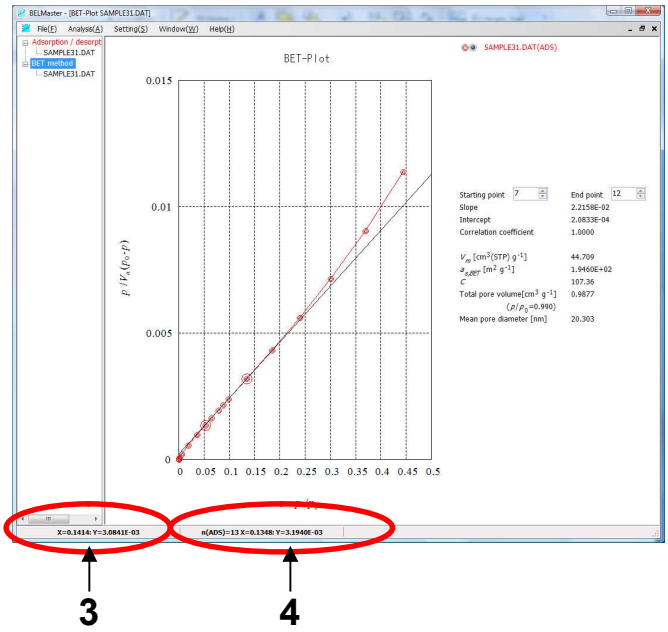
1. Select the plot data to display. When more than two data curves are displayed on the same graph, click the check box of each data set whose coordinates you want to display.

2. Move the pointer to the plot data set whose coordinate values you want to display, and click the left mouse button while pressing the [Alt] key.



3. The coordinates of the position you clicked on are shown on the left of the status bar (bottom bar on the screen).

4. The data number of the data nearest to the position you clicked on, and its coordinates, are displayed on the right side of the status bar.

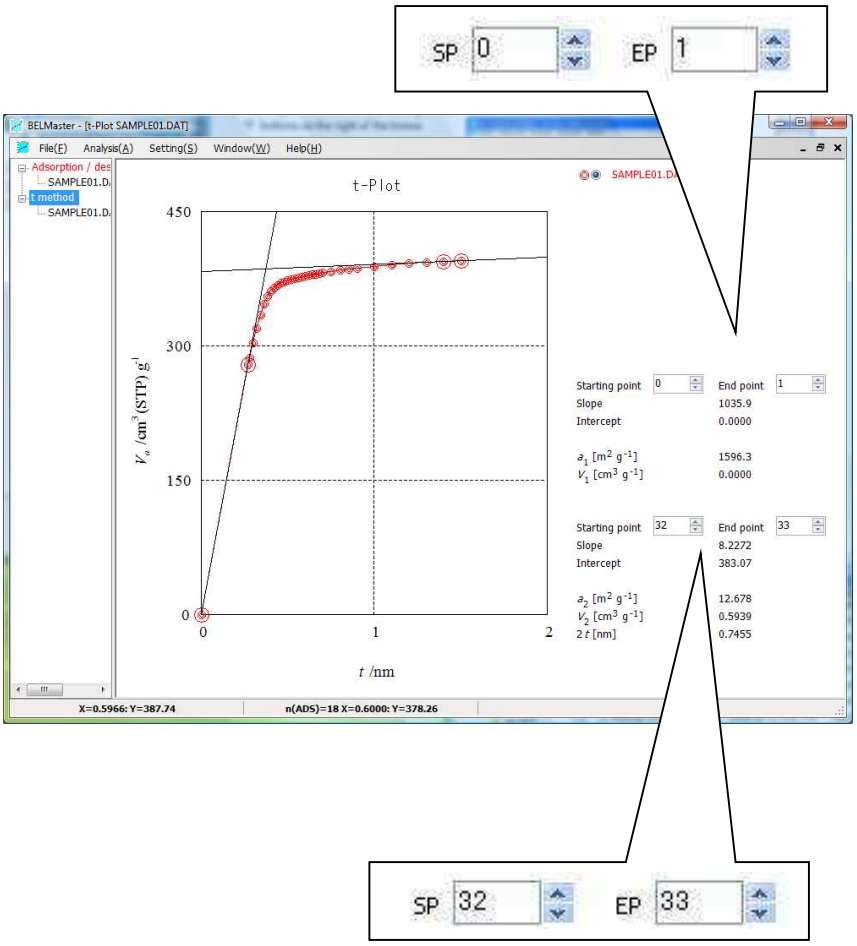


8-2. Setting the linear regression start and end points.

1. When analyses use the linear regression function (e.g. BET plot, Langmuir plot, t plot, α_s plot, DA plot, and metal distribution ratio), boxes will appear on the right of the graph to let you enter start and end points.

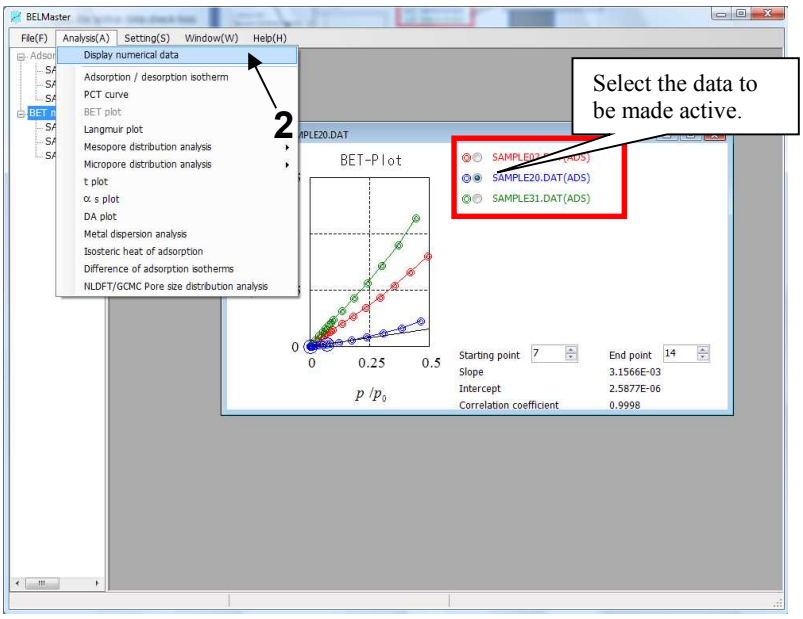
2. By changing these values, you can change the objective linear regression range. The numbers can be changed by entering a new value or by pressing the △▽ buttons on the right of the boxes.

3. If you want to delete a line, enter the same value for both the start and end points. The line will be deleted.



8-3. Displaying numerical data from a graph

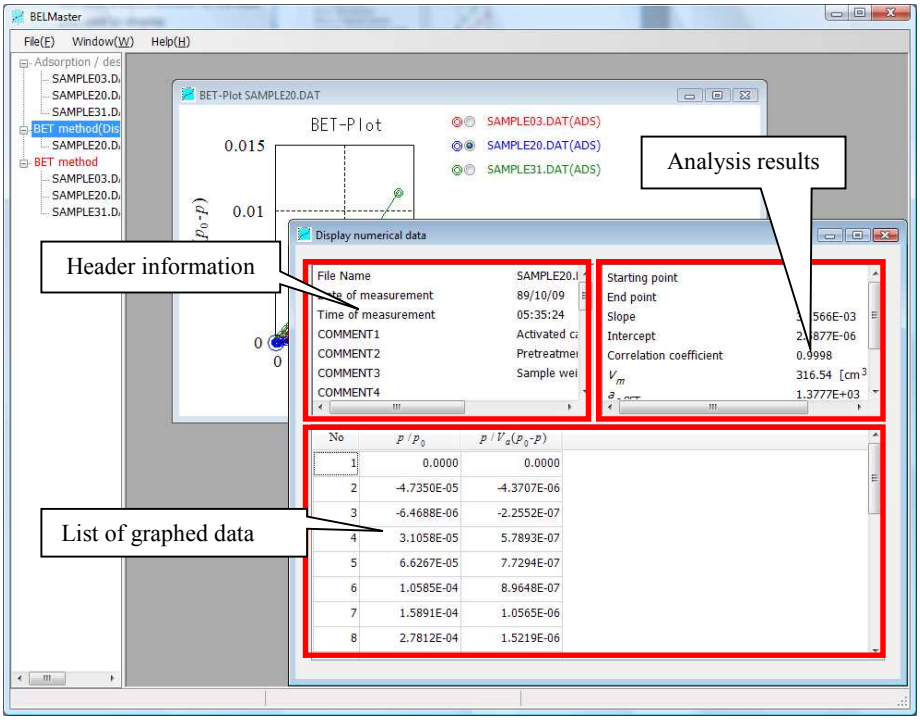
This function displays the numerical data for the graph data currently being analyzed.



1. Click the active data check box on the data analysis window for the data you want to display.

2. Select “Analysis (A)” and “Display numerical data” from the BEL analysis program menu, or move the cursor on the graph and click the right mouse button. Then select “Display numerical data” from the pop up menu.

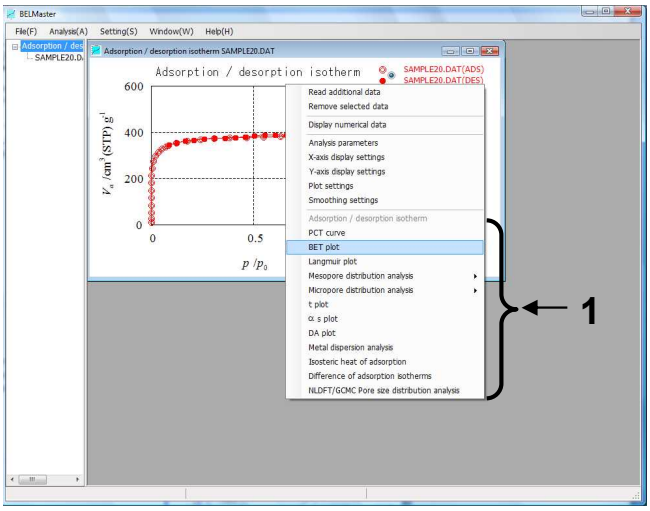
3. A new data analysis window will open and a list of the active data and header information will be displayed.



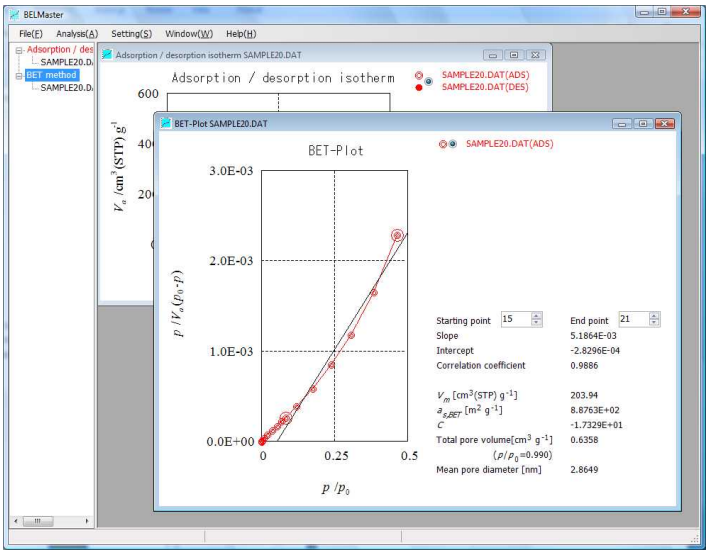
8-4. Analyze the active data by using another analysis method

The data for used in analysis methods other than the molecular probe method are based on a common format. Therefore, the data already opened can be analyzed with other analysis methods.

1. Move the cursor on the graph of the data analysis window and click the right mouse button. Or, select "Analysis (A)" from the BEL analysis program menu. The analysis menu will appear.

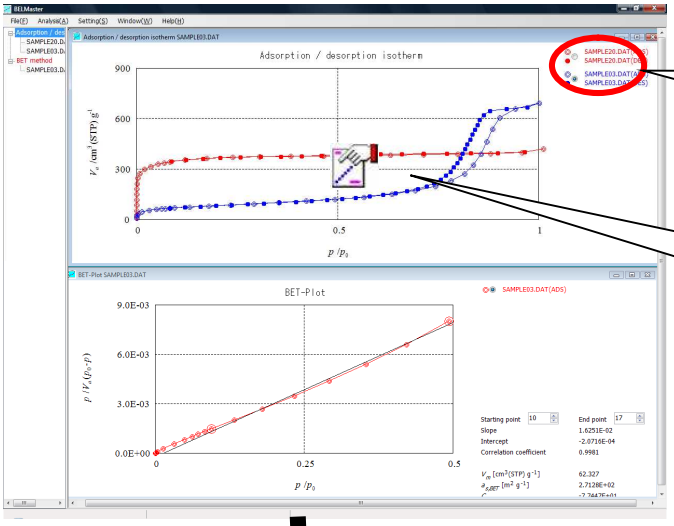


2. After selecting an analysis method, a new data analysis window will open. The program starts analysis of the data specified in the original graph. The figure below shows the results of executing a "BET analysis" from an "Adsorption / desorption isotherm".



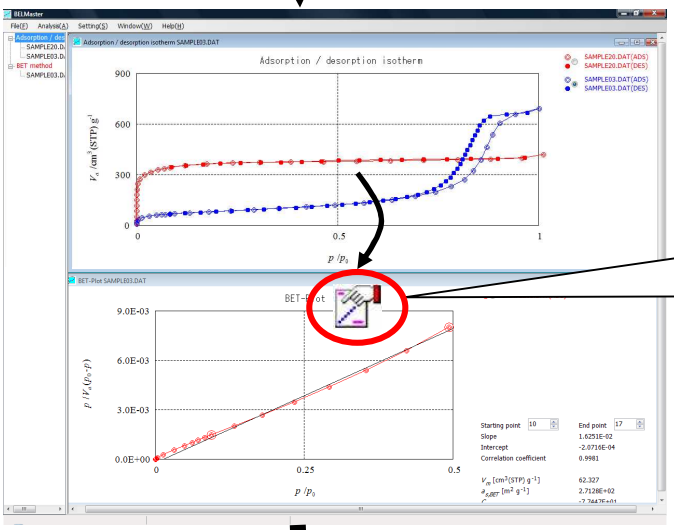
8-5. Transfer the data using the drag and drop function

When a data analysis window is already open, you can transfer the data by dragging and dropping the graph data.

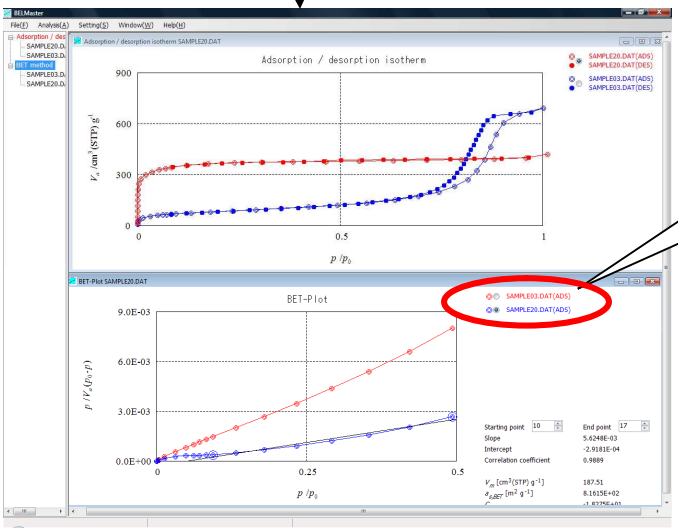


1. Confirm that data you want to transfer has been selected.

2. Move the cursor on the graph while holding down the left mouse button (The icon will change.).



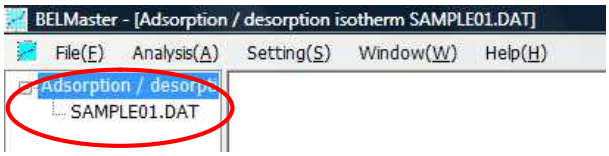
3. Move the cursor to the data analysis window you want to transfer data to while holding down the left mouse button. Then, release the left mouse button.



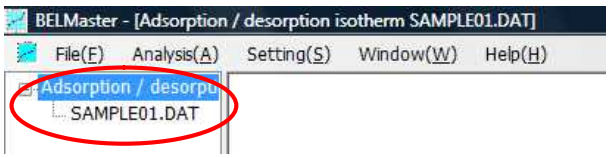
4. The data and graph will be added to that window.

8-6. Displaying the sub screen

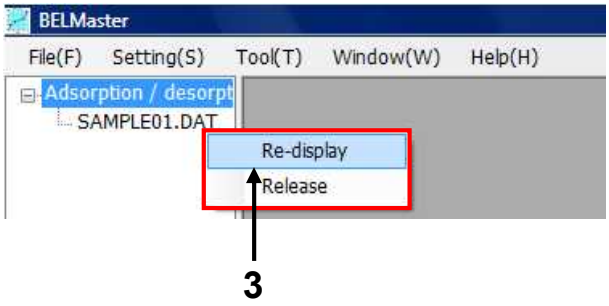
1. The file name for the currently analyzed graph data is displayed on the sub screen.



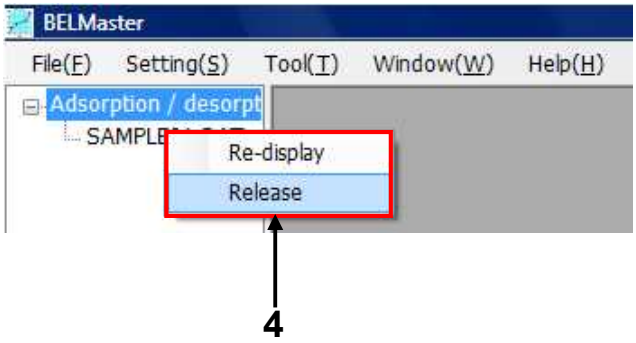
2. Even after graph data is deleted from the main screen, the analysis method and file name will be retained. (If you execute “Delete”, the analysis method and file name on the sub screen will be deleted.)



3. To re-display a graph after it is closed on the main screen, activate the analysis method for the data to be re-displayed on the sub screen (it will be displayed in blue), and click the mouse right button to show the window indicated as **3**. If you select “Re-display”, the relevant graph will be re-displayed.



4. To destroy data, activate the analysis method for the data to be destroyed on the sub screen (it will be displayed in blue), and click the mouse right button to show the window indicated as **4**. If you select “Destroy”, the relevant graph will be deleted.



Chapter 9: Saving and printing analysis results

Graphs and numerical data analyses can be saved in a file and printed on paper. This chapter describes how to save and print the analysis results. It also describes how to edit measured data (the measurement conditions for a sample weight) and it covers the help function.

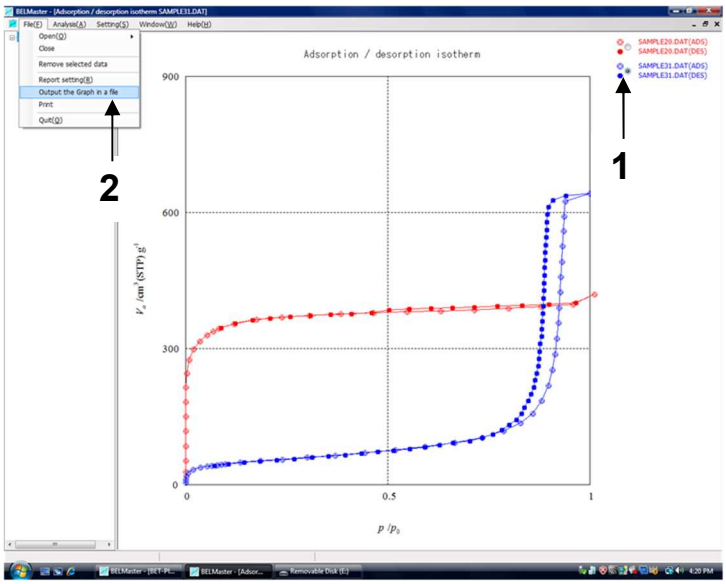
9-1. Save data analysis

1) Save data analysis (graph)

A data analysis graph can be saved as a bitmap file or a meta file. The saved image corresponds to the graphs output by selecting “File” and “Print”.

1. Make the analysis window of the graph you want to save active.

2. Select “File (F)” and then “Output the graph in a file” from the BEL analysis program menu.

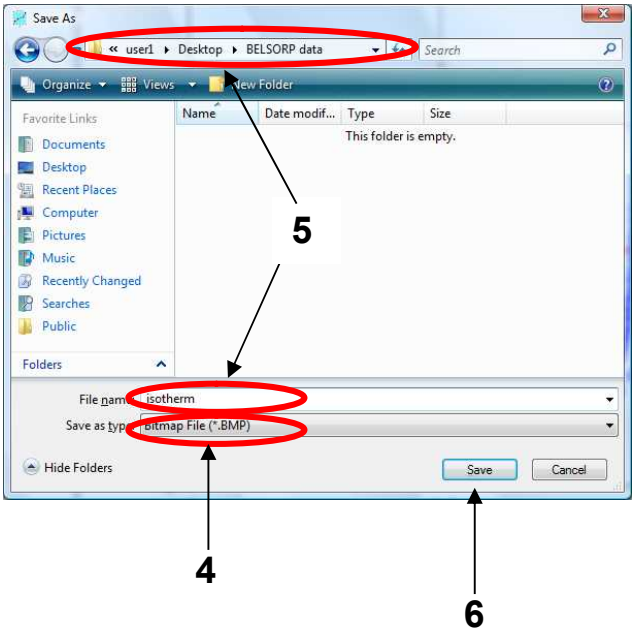


3. The “Save As” window shown on the right will appear.

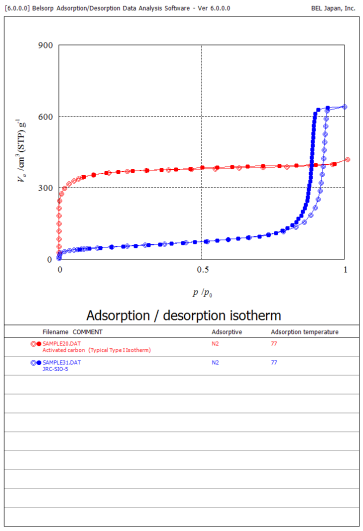
4. Select a file type (Bitmap File / Meta File).

5. Specify a folder to save the file in and enter a file name.

6. Click the [Save] button.
   The program will save the graph of the currently active data analysis window in a chiced file.



7. The figure on the right is an example of a graph that has been saved. It can be used with other programs.



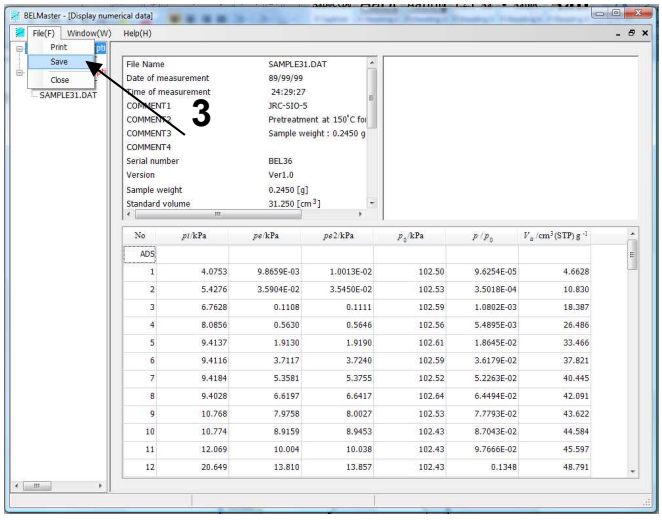
2) Save a data analysis (numerical data)

Numerical data from a data analysis can be saved in a file.

1. Display the numerical data you want to save.

[Reference]

Display numerical data => Display the numerical data in a graph, on page 35.



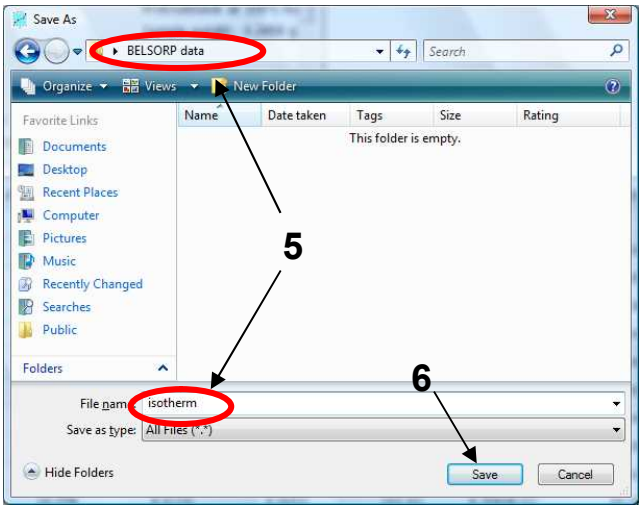
2. Select the analysis window that is displaying the numerical data to save.

3. Select “File (F)” and “Save” from the BEL analysis program menu.

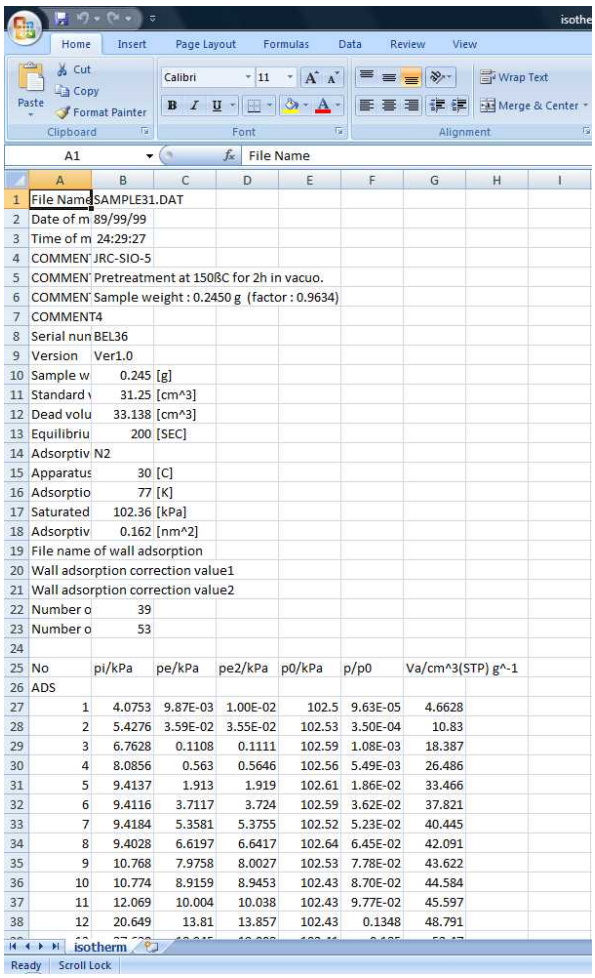
4. The “Save As” window shown on the right will appear.

5. Specify a folder to save the file in and enter a file name.

6. Click the [Save] button. The program will save the numerical data form the currently active data analysis window to a file.



7. The numerical data are stored in CSV format, so that they can be used with other programs. The figure on the right is an example of a numerical data file opened with Excel.



	A	B	C	D	E	F	G	H	I
1	File Name	SAMPLE31.DAT							
2	Date of m	89/99/99							
3	Time of m	24:29:27							
4	COMMEN	JRC-SIO-5							
5	COMMEN	Pretreatment at 150ßC for 2h in vacuo.							
6	COMMEN	Sample weight : 0.2450 g (factor : 0.9634)							
7	COMMENT4								
8	Serial nun	BEL36							
9	Version	Ver1.0							
10	Sample w	0.245	[g]						
11	Standard v	31.25	[cm^3]						
12	Dead volu	33.138	[cm^3]						
13	Equilibriu	200	[SEC]						
14	Adsorptiv	N2							
15	Apparatus	30	[C]						
16	Adsorptio	77	[K]						
17	Saturated	102.36	[kPa]						
18	Adsorptiv	0.162	[nm^2]						
19	File name of wall adsorption								
20	Wall adsorption correction value1								
21	Wall adsorption correction value2								
22	Number o	39							
23	Number o	53							
24									
25	No	pi/kPa	pe/kPa	pe2/kPa	p0/kPa	p/p0	Va/cm^3(STP) g^-1		
26	ADS								
27	1	4.0753	9.87E-03	1.00E-02	102.5	9.63E-05	4.6628		
28	2	5.4276	3.59E-02	3.55E-02	102.53	3.50E-04	10.83		
29	3	6.7628	0.1108	0.1111	102.59	1.08E-03	18.387		
30	4	8.0856	0.563	0.5646	102.56	5.49E-03	26.486		
31	5	9.4137	1.913	1.919	102.61	1.86E-02	33.466		
32	6	9.4116	3.7117	3.724	102.59	3.62E-02	37.821		
33	7	9.4184	5.3581	5.3755	102.52	5.23E-02	40.445		
34	8	9.4028	6.6197	6.6417	102.64	6.45E-02	42.091		
35	9	10.768	7.9758	8.0027	102.53	7.78E-02	43.622		
36	10	10.774	8.9159	8.9453	102.43	8.70E-02	44.584		
37	11	12.069	10.004	10.038	102.43	9.77E-02	45.597		
38	12	20.649	13.81	13.857	102.43	0.1348	48.791		

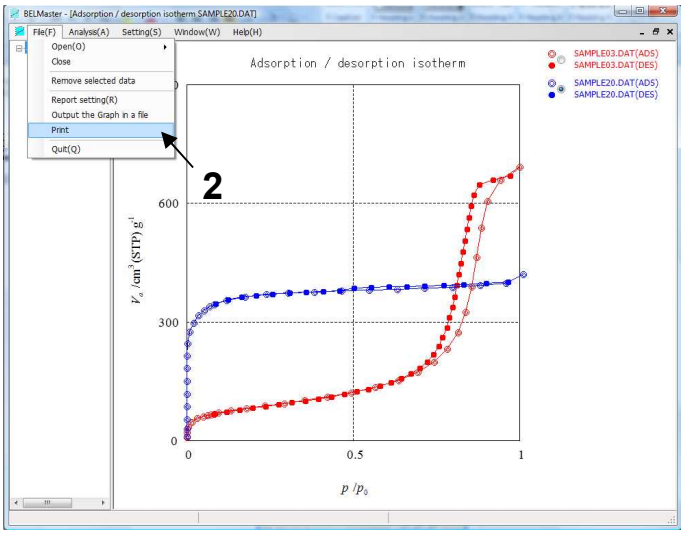
9-2. Printing a data analysis

1) Print a data analysis (graph)

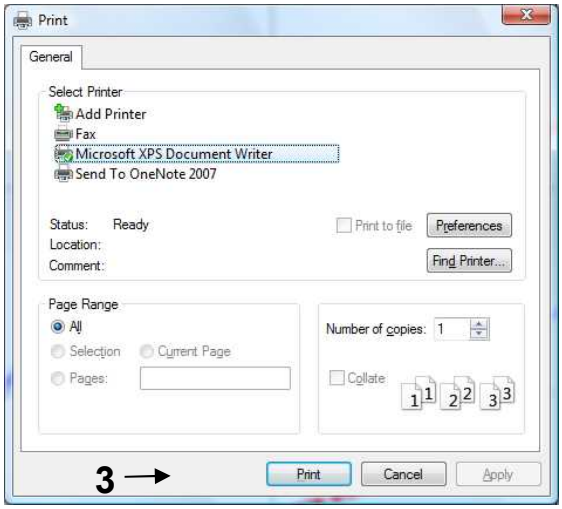
A graph of a data analysis can be printed on paper.

1. Select the analysis window containing the graph you want to print.

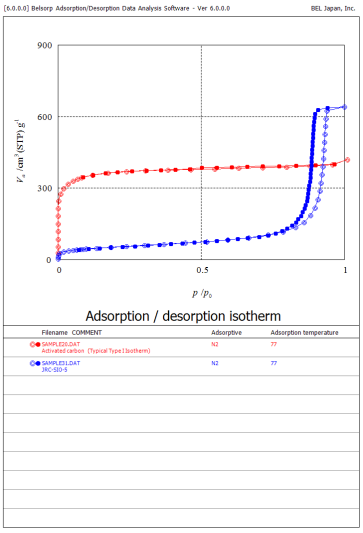
2. Select “File (F)” and “Print” from the BEL analysis program menu.



3. The “Print settings” window shown on the right will appear. Specify a printer type and print direction. Then click the [Print] button. The program will print the specified graph.



4. The data analysis (figure) are printed using the format shown on the right.



2) Print data analysis (numerical data)

Numerical data from a data analysis can be printed.

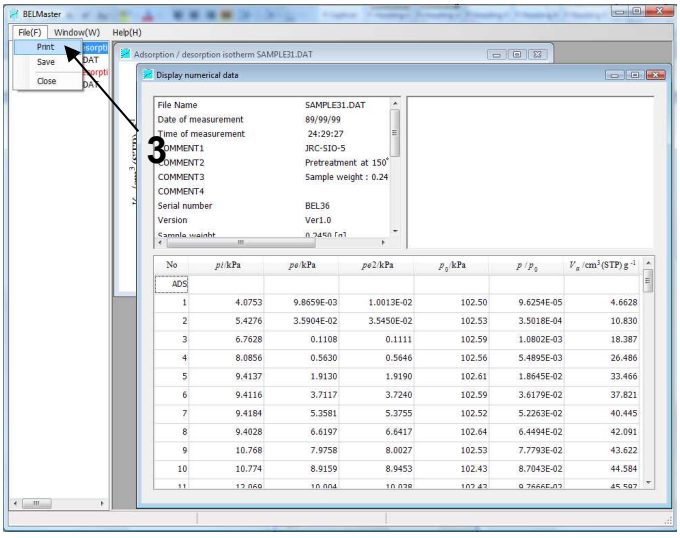
1. Display the numerical data you want to print.

[Reference]

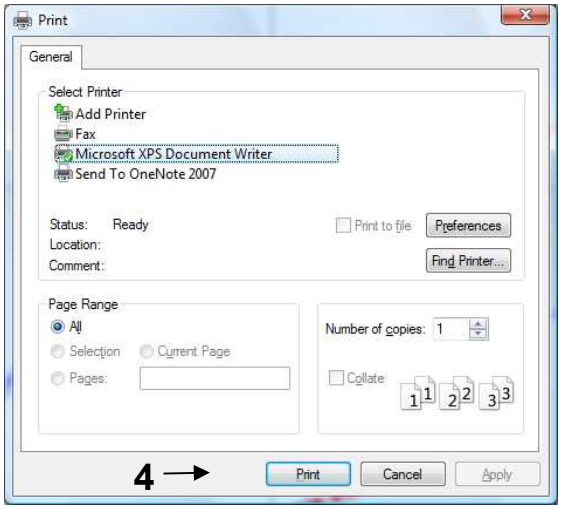
Display numerical data => Display the numerical data from a graph, on page 35.

2. Select the analysis window that is displaying the numerical data you want to print.

3. Select “File (F)” and “Print” from the BEL analysis program menu.



4. The “Print settings” window shown on the right will appear. Specify a printer type and print direction. Then click the [Pront] button. The program will print the specified numerical data.



5. Numerical data are printed using the format shown on the right.

[5.0.0.1] Belsorp Adsorption/Desorption Data Analysis Software — BEL Japan, Inc.

Adsorption / desorption isotherm (1/2)

Filename	SAMPLE31.DAT
COMMENT1	JRC-SIO-5
COMMENT2	Pretreatment at 150℃ for 2h in vacuo.
COMMENT3	Sample weight : 0.2450 g (factor : 0.9634)
COMMENT4	

Date of measurement	89/99/99	Time of measurement	24:29:27
Adsorbate	N2	Sample weight	0.2450 [g]
Adsorption temperature	77.000[K]	Adsorbate moleculer weight	28.010
Sample moleculer weight	0.0000	Sample surface area	0.0000 [m^2 g^{-1}]

[Adsorption branch]39Point

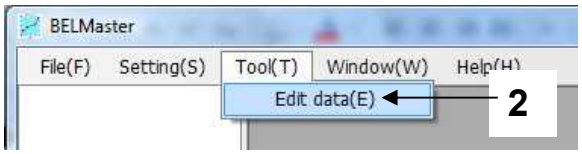
No	p_i /kPa	p_e /kPa	p_{e2} /kPa	p_0 /kPa	p / p_0	V_a /cm^3(STP) g^{-1}
1	4.0753	9.8659E-03	1.0013E-02	102.50	9.6254E-05	4.6628
2	5.4276	3.5904E-02	3.5450E-02	102.53	3.5018E-04	10.830
3	6.7628	0.1108	0.1111	102.59	1.0802E-03	18.387
4	8.0856	0.5630	0.5646	102.56	5.4895E-03	26.486
5	9.4137	1.9130	1.9190	102.61	1.8645E-02	33.466
6	9.4116	3.7117	3.7240	102.59	3.6179E-02	37.821
7	9.4184	5.3581	5.3755	102.52	5.2263E-02	40.445
8	9.4028	6.6197	6.6417	102.64	6.4494E-02	42.091
9	10.768	7.9758	8.0027	102.53	7.7793E-02	43.622
10	10.774	8.9159	8.9453	102.43	8.7043E-02	44.584
11	12.069	10.004	10.038	102.43	9.7666E-02	45.597
12	20.649	13.810	13.857	102.43	0.1348	48.791
13	27.628	18.945	19.008	102.41	0.1850	52.470

9-3. Edit data

The data items that were set when taking measurements can be edited and saved (sample, adsorptive, and measurement conditions).

1. Data editing is only possible when the “initial menu” window is displayed. If a data analysis window (graph or numerical data) is open, you cannot edit the data. Close any open data analysis windows and try editing the data again.

2. Select “Tool (T)” and “Edit data (E)” from the analysis program initial menu.



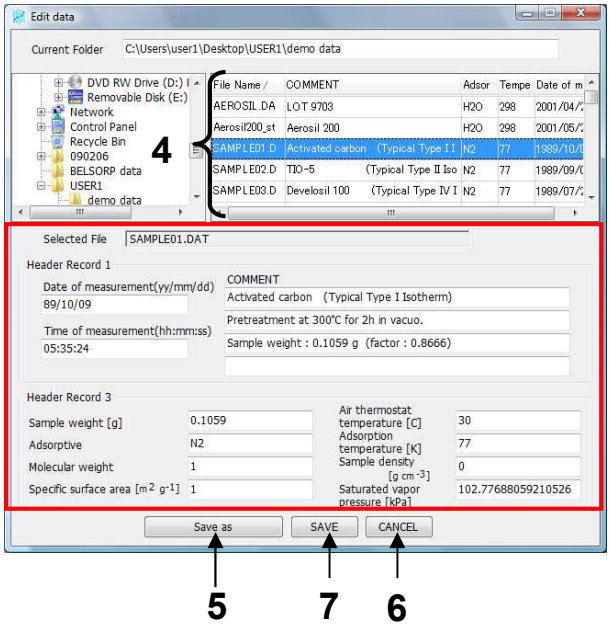
3. The “Edit data” window shown on the right will appear.

4. Select the file you want to edit from the list of data files.

5. The data items specified when measurements were taken will be displayed. Edit any item you want to change.

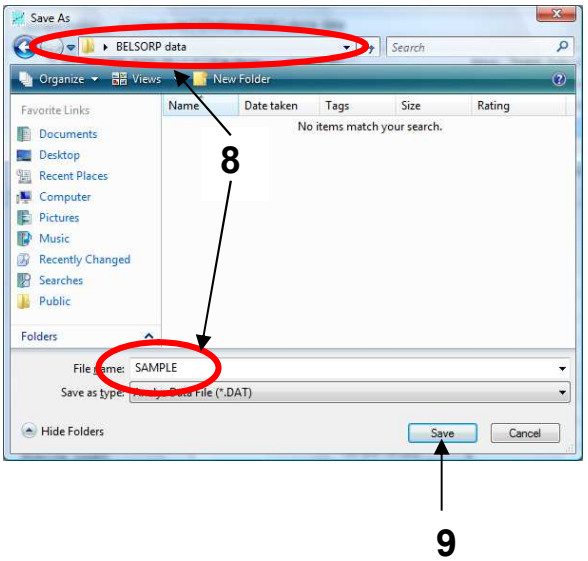
6. If you want to overwrite the existing file, click the [SAVE] button. An overwrite message window will appear. Select [Yes] and the program will overwrite the items that you changed.

7. To save it as a different file, click the [SAVE] button.



8. The “Save As” window shown on the right will appear. Specify a location to save the file in and enter a file name.

9. Click the [Save] button. The program will save the data using the file name you entered.

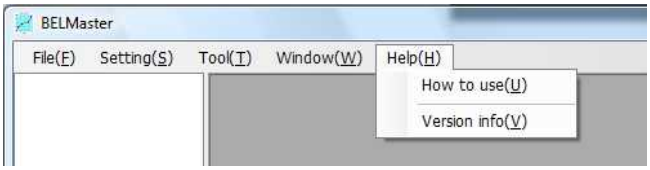


9-4. Help function

1) "How to use" this program

You can find instructions about various operation methods of the analysis program using the help function.

1. Select "Help (H)" and "How to use (U)" from the BEL analysis program menu.



2. The "BEL analysis software HELP" window appears. Here you can find descriptions of the operations and other details of the analysis program.

2) "Version info." of the analysis software

1. You can see the version information of the analysis program.

2. Select "Help (H)" and "Version info (V)" from the BEL analysis software menu.

3. The version information display screen shown on the right will appear.

Analysis of measured data

Chapter 10: Analysis of adsorption/desorption isotherms

The “BELSORP” series employs the volumetric theory to measure adsorption isotherms. It can produce reliable precision measurement data by setting appropriate measurement conditions. The adsorption amount relative to the pressure can be obtained as measured data. The relationship between them is referred to as an adsorption isotherm. This chapter briefly sums up the features of the adsorption isotherm and its analysis. Chapter 11 and later describe the operation methods while showing descriptions and sample examples for each analysis method.

10-1. Adsorption isotherm

In physical adsorption, adsorption isotherms can be classified as one of 6 types, as shown in the table below. Table 1 shows the types and features, as well an adsorbent example.

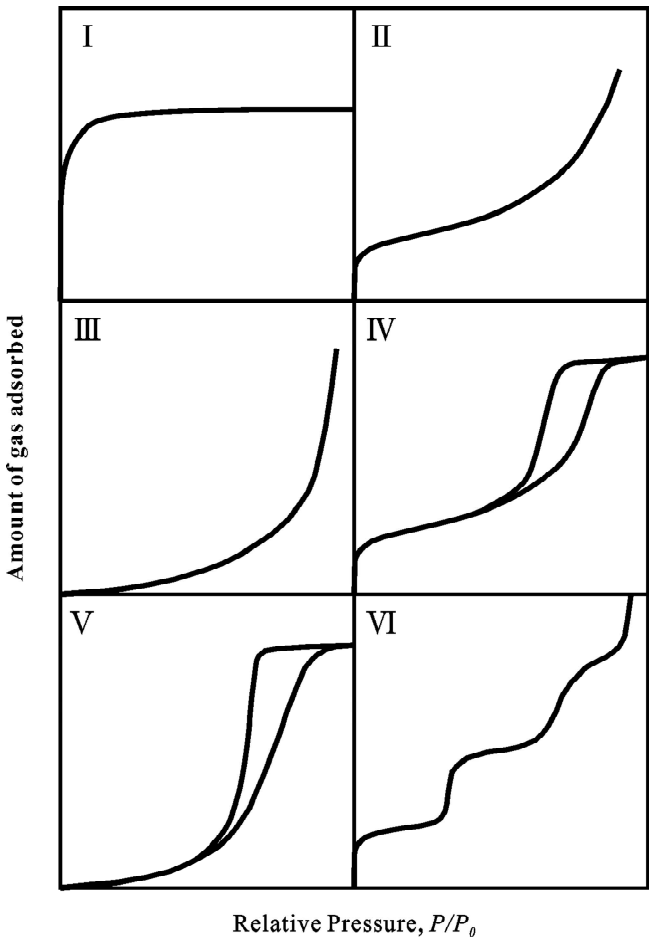


Figure 1: IUPAC classification of adsorption isotherms

Table 1: Features of adsorption isotherms

Type	Features		Sample – Adsorptive example
	Interaction between sample surface and adsorbate	Porosity	
I	Relatively strong	Micropores	Activated carbon - Nitrogen
II	Relatively strong	Nonporous	Oxide - Nitrogen
III	Weak	Nonporous	Carbon – Water vapor
IV	Relatively strong	Mesopore	Silica – Nitrogen
V	Weak	Mesopore	
		Micropore	Activated carbon – Water vapor
VI	Relatively strong Sample surface has an even distribution of energy	Nonporous	Graphite - Krypton

Size of pores is classified as shown in table 2 below.

Table 2: IUPAC classification of pores

	Pore diameter / nm
Micropore	Up to 2
Mesopore	2 to 50
Macropore	50 or up

Adsorption isotherms are classified as shown in table 2 based on the strength of the interaction between the sample surface and adsorptive, and the existence or absence of pores. However, some actual samples do not fit into adsorption isotherm types I to IV. These may be measured as mixed types of adsorption isotherms. For example, nitrogen adsorption for a porous sample with large external surface area may generate a compound isotherm resembling types I and II, or types I and IV. To analyze an adsorption isotherm, you have to assume certain sample features, such as the pores from the shape of the isotherm. Then you can analyze them using an appropriate analysis method.

«Reference»

- "Adsorption Surface Area and Porosity", 2nd Ed., S. J. Gregg & K. S. W. Sing, Academic Press INC., London (1982).
- "Adsorption by Powders and Porous Solids", F. Rouquerol, J Rouquerol & K. S. W. Sing, Academic Press INC., London (1999).

10-2. Analysis data obtained from a nitrogen adsorption isotherm

By measuring nitrogen adsorption isotherms, a type I, II, or IV adsorption isotherm can be measured mainly and sample information concerning a specific surface area and porous structure will be obtained. Table 3 briefly sums up what analysis data can be obtained from a nitrogen adsorption isotherm.

Table 3: Analysis data obtained from a nitrogen adsorption isotherm

Type of adsorption isotherm	Sample information	Analysis method	Major analyzed data	Remark
Type I	Total specific surface area	BET plot	$a_{s,BET}$ [$m^2 g^{-1}$]	Needs careful evaluation of the analysis results.
	Total specific surface area	*t* plot, α_s plot	a_1 [$m^2 g^{-1}$]	
	External specific surface area	*t* plot, α_s plot	a_2 [$m^2 g^{-1}$]	
	Micropore area	*t* plot, α_s plot	a_1-a_2 [$m^2 g^{-1}$]	
	Micropore volume	*t* plot, α_s plot	V_2 [$cm^3 g^{-1}$]	
	Micropore width	*t* plot	2*t* [nm]	Pore shape: Slit Pore dia.: 0.7 to 1.0 nm
	Micropore distribution curve	MP plot	Micropore range	
	Micropore distribution peak	MP plot	$d_{p\ peak}$ or $r_{p\ peak}$ [nm]	
	Micropore volume	DA plot	V_p [$cm^3 g^{-1}$]	
	Micropore distribution curve	HK plot	Micropore range	Pore shape: Slit Pore dia.: 1.0 nm or less
	Micropore distribution peak	HK plot	$d_{p\ peak}$ or $r_{p\ peak}$ [nm]	
	Micropore distribution curve	SF plot	Micropore range	Pore shape: Cylinder Pore dia.: 1.0 nm or less
	Micropore distribution peak	SF plot	$d_{p\ peak}$ or $r_{p\ peak}$ [nm]	
Type II	Total specific surface area	BET plot	$a_{s,BET}$ [$m^2 g^{-1}$]	
	Total specific surface area	*t* plot, α_s plot	a_1 [$m^2 g^{-1}$]	
Type IV	Total specific surface area	BET plot	$a_{s,BET}$ [$m^2 g^{-1}$]	
	Total specific surface area	*t* plot, α_s plot	a_1 [$m^2 g^{-1}$]	
	Mesopore distribution curve	BJH plot, DH plot, CI plot	Mesopore range	
	Mesopore distribution peak	BJH plot, DH plot, CI plot,INNES plot	$d_{p\ peak}$ or $r_{p\ peak}$ [nm]	
	Mesopore volume	BJH plot, DH plot, CI plot,INNES plot	V_p [$cm^3 g^{-1}$]	
	Mesopore area	BJH plot, DH plot, CI plot,INNES plot	a_p [$m^2 g^{-1}$]	

Table 4 sums up symbols used in section 11 or later.

Table 4: Using symbols in the BELMaster manual

Method	Symbol	Unit	Mean
Adsorption / desorption isotherm	p/p_0	–	Relative pressure (p_0 is saturation pressure of the adsorptive at measurement temperature.)
	p	kPa, Torr	Absolute pressure
	RH	%	Relative humidity
	V_a	$cm^3(STP)\ g^{-1}$	Specific amount adsorbed expressed in the gas volume at the standard state (STP: T=273.15 K, 101.3 kPa) on 1 g of adsorbent
	m_a	$mg\ g^{-1}$	Specific mass adsorbed on 1 g of adsorbent
	Γ	$molec\ nm^{-2}$	Numbers of molecules adsorbed on a unit surface area of adsorbent
	n_a	$mol\ mol^{-1}$	Amount adsorbed on 1 mol of adsorbent expressed in mol
	n_a	$mol\ g^{-1}$	Amount adsorbed on 1 g of adsorbent expressed in mol
	wt	%	Amount adsorbed on 1 g of adsorbed expressed in percentage
	α_s	–	A value obtained by dividing an adsorption amount at arbitrary equilibrium pressure by adsorption amount *Va (p/p_0 = 0.4)*.
PCT curve		-	Amount (mol) of hydrogen occluded by 1 mol of sample (metal).
	wt	%	Amount (%) of hydrogen occluded by 1 g of sample (metal).
	V_a	$cm^3(STP)\ g^{-1}$	Specific amount adsorbed expressed in the gas volume at the standard state (STP: T=273.15 K, 101.3 kPa) on 1 g of sample (metal).
	p	kPa, MPa, bar	Absolute pressure
BET analysis	p/p_0	–	Relative pressure (p_0 is saturation pressure of the adsorptive at measurement temperature.)
	V_m	$cm^3(STP)\ g^{-1}$	Monolayer volume
	a_{sBET}	$m^2\ g^{-1}$	BET specific surface area
	C	–	Energy constant (the first layer)
	σ	nm^2	Cross section area of an adsorptive area
	M_g	–	Molecular weight of adosorptive
	L	–	Avogadro number
	ρ_a	$g\ cm^{-3}$	Dencity of adosorptive
	ρ_s	$g\ cm^{-3}$	Dencity of sample
	V_p	$cm^3\ g^{-1}$	Total pore volume
	d_p	nm	Mean pore diameter
	l	nm	Mean particle size
Langmuir plot	P	kPa, Torr	Absolute pressure
	V_m	$cm^3(STP)\ g^{-1}$	Monolayer volume
	a_{sLang}	$m^2\ g^{-1}$	Langmuir specific surface area
	B	–	Ratio of rate constant (adsorption / desorption)
	σ	nm^2	Cross section area of an adsorptive area
T plot	t	nm	Thickness of adsorption layer
	a_1	$m^2\ g^{-1}$	Total specific surface area
	a_2	$m^2\ g^{-1}$	External surface area
	V_1	$cm^3\ g^{-1}$	Pore volume
	V_2	$cm^3\ g^{-1}$	Pore volume
	$2t$	nm	Pore diameter
	V_a	$cm^3(STP)\ g^{-1}$	Specific amount adsorbed expressed in the gas volume at the standard state (STP: T=273.15 K, 101.3 kPa) on 1 g of sample

Method	Symbol	Unit	Mean
α_s plot	α_s	—	Normalized adsorption n/ $n_{0.4}$
	V_a	$cm^3(STP)\ g^{-1}$	Specific amount adsorbed expressed in the gas volume at the standard state (STP: T=273.15 K, 101.3 kPa) on 1 g of sample
	A_1	$m^2\ g^{-1}$	Total specific surface area
	A_2	$m^2\ g^{-1}$	External surface area
	V_1	$cm^3\ g^{-1}$	Pore volume
	V_2	$cm^3\ g^{-1}$	Pore volume
MP plot	r_p	nm	Micropore radius
	d_p	nm	Micropore diameter
	dV_p / dr_p	$cm^3\ g^{-1}\ nm^{-1}$	Area distribution
	$dV_p / dlogr_p$	—	Volume distrribution
	dV_p / dd_p	$cm^3\ g^{-1}\ nm^{-1}$	Area distribution
	$dV_p / dlogd_p$	—	Volume distribution
	ΣV_p	$cm^3\ g^{-1}$	Integral curve
	a_1	$m^2\ g^{-1}$	Total specific surface area
	a_2	$m^2\ g^{-1}$	External surface area
	V_1	$cm^3\ g^{-1}$	Pore volume
	V_2	$cm^3\ g^{-1}$	Pore volume
BJH / CI / DH plot	r_p	nm	Micropore radius (cylindrical shape)
	d_p	nm	Micropore diameter (cylindrical shape)
	dV_p / dr_p	$cm^3\ g^{-1}\ nm^{-1}$	Area distribution
	$dV_p / dlogr_p$	—	Volume distribution
	dV_p / dd_p	$cm^3\ g^{-1}\ nm^{-1}$	Area distribution
	$dV_p / dlogd_p$	—	Volume distribution
	ΣV_p	$cm^3\ g^{-1}$	Integral curve
	A_p	$m^2\ g^{-1}$	Pore specific surface area
	V_p	$cm^3\ g^{-1}$	Pore Volume
INNES plot	d_x	nm	Slit pore radius (slit shape)
	dVp / ddx	$cm^3\ g^{-1}\ nm^{-1}$	Area distribution
	$dVp / dlogdx$	—	Volume distribution
	ΣV_p	$cm^3\ g^{-1}$	Integral curve
	a_p	$m^2\ g^{-1}$	The pore specific surface area
	V_p	$cm^3\ g^{-1}$	Pore volume
DA plot	V_p	$cm^3\ g^{-1}$	Pore Volume
	E_0	$kJ\ mol^{-1}$	Adsorption potential energy
HK plot	W	nm	Slit pore radius (slit shape)
	dV_p / dW	$cm^3\ g^{-1}\ nm^{-1}$	Area distribution
	$dV_p / dlogW$	—	Volume distribution
	ΣV_p	$cm^3\ g^{-1}$	Integral curve
	d_a	nm	Adsorptive molecular diameter
	d_s	nm	Adsorbent atom diameter
	N_a	m^{-2}	Number of adsorptive molecules adsorbed per unit surface area
	N_s	m^{-2}	Number of adsorbent atoms per unit surface area
	X_a	cm^3	Magnetic susceptibility of the adsorptive molecular
	X_s	cm^3	Magnetic susceptibility of the adsorbent atom
	α_a	cm^3	Polarizability of the adsorptive molecular
	α_s	cm^3	Polarizability of the adsorbent atom

Method	Symbol	Unit	Mean
SFplot	r_p	nm	Micropore radius (cylindrical shape)
	d_p	nm	Micropore diameter (cylindrical shape)
	dV_p/dr_p	$cm^3\ g^{-1}nm^{-1}$	Area distribution
	$dV_p/dlogr_p$	—	Volume distribution
	dV_p/dd_p	$cm^3\ g^{-1}nm^{-1}$	Area distribution
	$dV_p/dlogd_p$	—	Volume distribution
	ΣV_p	$cm^3\ g^{-1}$	Integral curve
	d_a	nm	Adsorptive molecular diameter
	d_s	nm	Adsorbent atom diameter
	N_a	m^{-2}	Number of adsorptive molecules adsorbed per unit surface area
	N_s	m^{-2}	Number of adsorbent atoms per unit surface area
	X_a	cm^3	Magnetic susceptibility of the adsorptive molecular
	X_s	cm^3	Magnetic susceptibility of the adsorbent atom
	α_a	cm^3	Polarizability of the adsorptive molecular
	α_s	cm^3	Polarizability of the adsorbent atom
Isosteric heat of adsorption	Q_{st}	kJ mol^{-1}	Isosteric heat of adsorption
	V_a	$cm^3(STP)g^{-1}$	Specific amount adsorbed expressed in the gas volume at the standard state (STP: T=273.15 K, 101.3 kPa) on 1 g of adsorbent.
Metal dispersion ration analysis	P	kPa,Torr	Absolute pressure
	V_a	$cm^3(STP)g^{-1}$	Specific amount adsorbed expressed in the gas volume at the standard state (STP: T=273.15 K, 101.3 kPa) on 1 g of adsorbent.
	N_g	mol g^{-1}	Number of molesof the gas that adsorbed on supported metal catalyst 1 g
	N_s	mol g^{-1}	Number of metal atoms on the metal catalyst 1 g
	N_T	mol g^{-1}	Number of moles of metal atom per catalyst 1 g
	C	%	Metal loading
	k_{sf}	—	Stoichiometry factor
	D_m	%	Metal dispersion ratio
	a_m	$nm^2\ atm^{-1}$	Cross section area that a supported metal atom occupies (supported metal cross section area)
	a_s *(sample)*	$m^2\ g^{-1}$	Supported metal surface area per supported metal 1 g
	a_s *(Metal)*	$m^2\ g^{-1}$	Supported metal surface area per supported metal 1 g
	l_m	nm	Metal particle size
Molecular probe method	r_p	nm	Micropore radius
	d_p	nm	Micropore diameter
	Vp	$cm^3\ g^{-1}$	Pore volume
	W_0	$cm^3\ g^{-1}$	Pore volume
	D_S	nm	Minor axis length of smallest projection cross section area (adsorptive)
	D_L	nm	Major axis length of smallest projection cross section area (adsorptive)
	d_m	nm	Adsorptive molecular
NLDFT/GCMC	d_p	nm	Pore diameter (cylindrical shape)
	W	nm	Pore width (slit shape)
	d_s	nm	Adsorbent atom diameter
	Vp	$cm^3\ g^{-1}$	Pore volume
	dVp	$cm^3\ g^{-1}$	Change of Pore volume
	ΣV_p	$cm^3\ g^{-1}$	Integral curve
	dV_p/dr_p	$cm^3\ g^{-1}nm^{-1}$	Area distribution
	$dV_p/dlogr_p$	—	Volume distribution
	dV_p/dd_p	$cm^3\ g^{-1}nm^{-1}$	Area distribution
	$dV_p/dlogd_p$	—	Volume distribution
	dSp	$m^2\ g^{-1}$	Change of Pore surface area
	ΣSp	$m^2\ g^{-1}$	Integral curve of surface area

Chapter 11: Adsorption / desorption isotherm

11-1. Description

The adsorption / desorption isotherm shows the relationship between the amount of adsorbed/desorbed gas (y-axis) and the pressure of adsorptive (x-axis) at the constant temperature. In our software, user can select the desired x-axis unit among four. In measurement data, $p(i)$, the pressure of ith measurement point is expressed in kPa. X-coordinate value can be calculated as follows.

In case "p/p_0" is selected:

$$x(i) = p(i) / p_0(i)$$

(Where $p_0(i)$ / kPa is saturation pressure of the adsorptive at measurement temperature.)

In case "p / kPa" is selected:

$$x(i) = p(i)$$

In case "p / Torr[*1]" is selected:

$$x(i) = p(i) / 101.325 \times 760$$

In case "RH / %" is selected:

$$x(i) = p(i) / p_0(i) \times 100$$

And also user can select the desired y-axis units among five listed below.

In case "V_a /cm^3(STP) g^{-1} [*2]" is selected:

$$y(i) = v(i)$$

In case "m_a / mg g^{-1} [*3]" is selected:

$$y(i) = v(i) / 22414 \times M_g$$

(Where M_g is moleculer weight of adsorptive.)

In case "Γ/ molec nm^{-2} [*4]" is selected:

$$y(i) = v(i) / 22414 \times 6.022 \times 10^{23} / a_s \times 10^{-18}$$

(Where a_s/m^2 g^{-1} is the specific surface area of adsorbent.)

In case "n_a / mol mol^{-1} [*5]" is selected:

$$y(i) = v(i) / 22414 \times M_s$$

(Where M_s is moleculer weight of sample.)

In case n_a / mol g^{-1} [*6] is selected:

$$y(i) = v(i) / 22414$$

In case *wt* / % [*7] is selected:

$$y(i) = v(i) / 22414 \times M_g \times 100$$

In case α_s [*8] is selected:

$$y(i) = v(i) / \left(v(p / p_0 = 0.4)\right)$$

(Where *v (p/p0=0.4)* is the adosorption volume of the p/p0=0.4.)

*1: Though "Torr" is not included in ISO system of units, it is commonly used even today. Users can choose it in our software. Pay attention when you use "Torr" in official documents.

*2: "V_a / ml(STP) g^{-1}" is the specific amount adsorbed expressed in the gas volume at the standard state(STP : T=273.15 K and P=101.3 kPa).

*3: "m_a / mg g^{-1}" is the specific mass adsorbed.

*4: "Γ/ molec nm^{-2}" is the number of molecules adsorbed on a unit surface area of adsorbent.

*5: "n_a / mol mol^{-1}" is the amount adsorbed on 1mol of adsorbent expressed in mol.

*6: "n_a / mol g^{-1}" is the specific amount adsorbed expressed in mol.

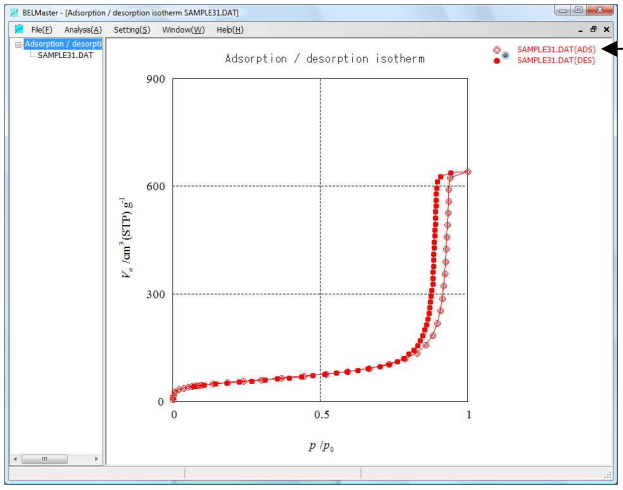
*7: "*wt/%*" is percentage of weight of adsorption per gram of sample.

*8: A value obtained by dividing an adsorption amount at arbitrary equilibrium pressure by adsorption amount *Va (p/p0 = 0.4)*

11-2. Operation

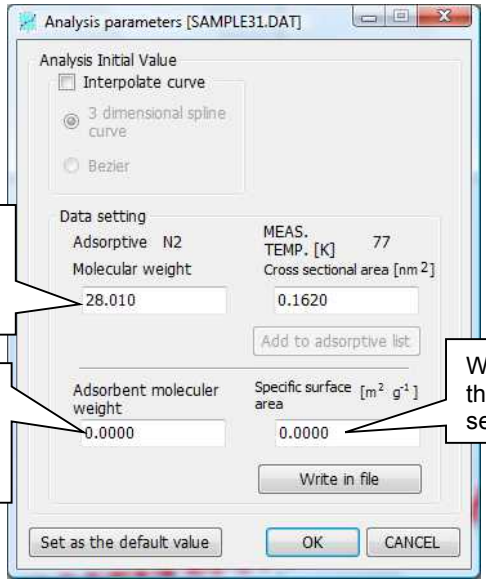
1. On the BEL analysis software menu, select “adsorption/desorption isotherm”. The program will display the following adsorption/desorption isotherm. For details about how to read the data, see “Chapter 6: Reading analysis data”, on page 30.

2. “ADS” next to a data name means that it is data from an adsorption process and “DES” next to a data name means that it is desorption data.



2

3. Select “Analysis parameters” on the “Settings” menu and the “Analysis parameters” window shown below will appear. Change the settings as needed.



When “m_a/mg g^{-1}” is selected as the Y axis unit in “Y axis display settings”, this value must be entered.

When “n_a/mol mol^{-1}” is selected as the Y axis unit in “Y axis display settings”, this value must be entered.

When “Γ/molec mn^{-2}” is selected as the Y axis unit in “Y axis display settings”, this value must be entered.

Chapter 12: PCT curve

12-1. Description

PCT curve (Pressure-Composition-Isotherm) is a graph that shows relationship between the amount of hydrogen occluded by hydrogen occlusion alloy at a constant temperature (x-coordinate) and the hydrogen pressure (y-coordinate). When the amount of hydrogen occluded at the i-th point in measurement data is indicated as "v(i) cm^3 (STP) g^{-1}", the x-coordinate (x (i)) can be obtained with the equation below.

When "H/M"*1 is selected:

$$x(i) = 2 \times v(i) \times M_{metal} / 22414$$

(M_{metal}: Molecular weight of metal)

When "wt%"*2 is selected:

$$x(i) = v(i) / 22414 \times M_g \times 100$$

(Where M_g is moleculer weight of adsorptive.)

When "cm^3 (STP) g^{-1}"*3 is selected:

$$x(i) = v(i)$$

When pressure at the i-th point in measurement data is indicated as "P(i) kPa", y coordinate (y (i)) can be obtained with the equation below.

When "p / kPa" is selected:

$$y(i) = p(i)$$

When "MPa / kPa" is selected:

$$y(i) = p(i) / 1000$$

When "p / bar" is selected:

$$y(i) = p(i) / 100$$

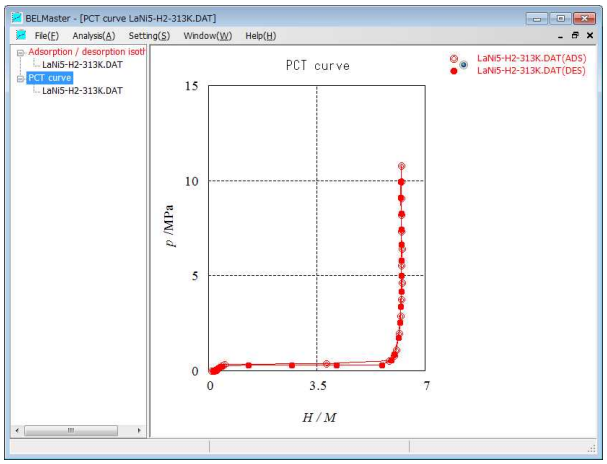
*1: Amount (mol) of hydrogen occluded by 1 mol of sample (metal).

*2: Amount (%) of hydrogen occluded by 1 g of sample (metal).

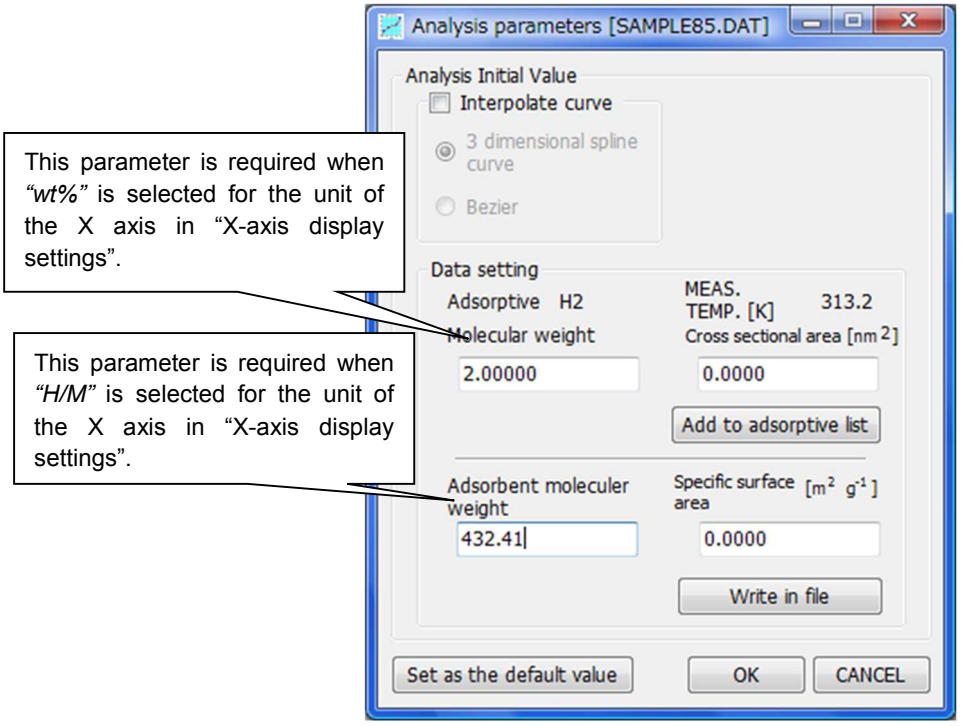
*3: Volume of gas at 0 °C and 101.325 kPa, converted from amount of adsorption by 1 g of sample (metal).

12-2. Operaion

1. If you select “PCT curve” from the menu of the analysis software, a PCT curve is displayed as shown below. For the data loading procedure, refer to page 30.



2. If you select “Analysis setting” from the “Setting” menu, the “Analysis parameters” window appears as shown below. Change the parameter settings as required.



This parameter is required when *“wt%”* is selected for the unit of the X axis in “X-axis display settings”.

This parameter is required when *“H/M”* is selected for the unit of the X axis in “X-axis display settings”.

Chapter 13: BET analysis

13-1. Description

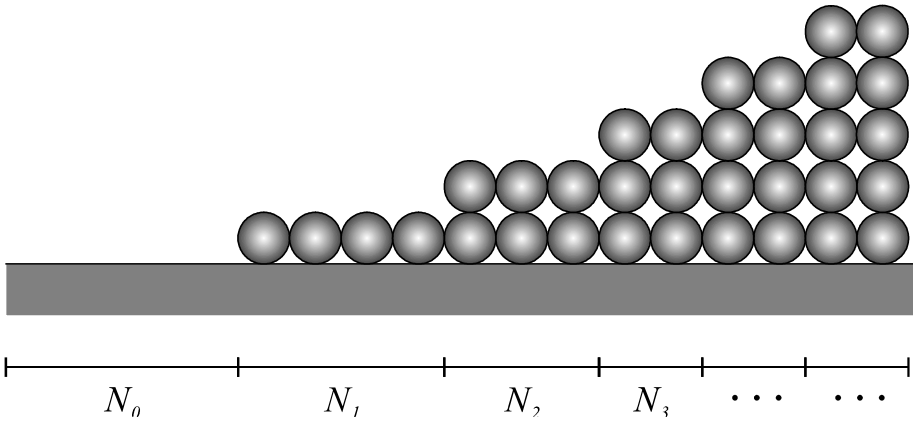
13-1-1. BET Theory

In 1938, Brunauer, Emmett and Teller reported the multilayer adsorption theory (BET theory). They extended the Langmuir's monolayer theory to multilayer adsorption. The derived equation is named the BET equation after the first letter of each of their names. The BET equation has been utilized in determining the monolayer volume of adsorbed gas, from which we can calculate the surface area of adsorbent.

The BET equation was derived on the following hypotheses:

1) Surface is energetically homogeneous; *i.e.,* all adsorption sites on bare solid surface have the same adsorption energy(E_1).
2) There is no lateral interaction between adsorbed molecules.
3) The adsorption energies in the second and all higher layers (E_2, E_3…) are equal to condensation energy of adsorptive (E_L) ; i.e., $E_2=E_3=.....=E_i=E_L$.

The BET adsorption model is shown below, where $N_0,N_1,N_2,N_3.....N_i,.....$ represent the adsorption sites that are covered by 0, 1, 2, 3, …, i,… layers of adsorbed molecules. At adsorption equilibrium, $N_0,N_1,N_2,N_3.....N_i,.....$ must remain constant.



First, we consider the case of i=0. N_0 decreases when adsorption occurs on the bare surface and the adsorption rate is proportional to N_0. N_0 increases when desorption occurs from the first layer and the desorption rate is proportional to N_1. Because N_0=constant at adsorption equilibrium, the adsorption rate is equal to the desorption rate; therefore, Equation (13.1) is obtained.

$$a_1 p N_0 = b_1 N_1 \exp\left(-\frac{E_1}{RT}\right) \tag{13.1}$$

Next, we consider the case of i=1, where the four processes are included; namely, (a) the adsorption of gas molecules to the bare solid surface, (b) the desorption of adsorbed molecules from the second adsorbed layer, (c) the adsorption of gas molecules to the first adsorbed layer, and (d) the desorption of adsorbed molecules from the first adsorbed layer. At adsorption equilibrium, the rate of formation of the first adsobed layer, which is the rate of (a) and (b), is equal to the rate of disappearance of the first adsorbed layer, which is the rate of (c) and (d). Therefore, the following equation is obtained:

$$a_1 p N_0 + b_2 N_2 \exp\left(\frac{-E_2}{RT}\right) = a_2 p N_1 + b_1 N_1 \left(\frac{-E_1}{RT}\right) \tag{13.2}$$

Equation (13.3) is obtained by substituting equation (13.1) into equation (13.2),

$$a_2 p N_1 = b_2 N_2 \exp\left(-\frac{E_2}{RT}\right) \tag{13.3}$$

Extending the same argument to the *i* th layer (N_i = constant), equation (13.4) can be derived.

$$a_i p N_{i-1} = b_i N_i \exp\left(-\frac{E_i}{RT}\right) \tag{13.4}$$

Equation (13.4) is tranformed into equation (13.5).

$$N_i = \frac{a_i}{b_i} p N_{i-1} \exp\left(-\frac{E_i}{RT}\right) \tag{13.5}$$

Equation (13.6) may be obtained if the adsorption behavior of gas is same for higher than the second layer,

$$g = \frac{b_2}{a_2} = \frac{b_3}{a_3} = \cdots = \frac{b_i}{a_i} \tag{13.6}$$

From both of equation (13.6) and hypothesis 3), Equation (13.5) can be transformed into equation (13.7) and equation (13.8) when $i \geq 2$:

$$N_i = \frac{p}{g} N_{i-1} \exp\left(\frac{E_L}{RT}\right) \tag{13.7}$$

Here, we define x as follows:

$$x = \frac{p}{g} \exp\left(\frac{E_L}{RT}\right) \tag{13.8}$$

By inserting equations (12.8) into Equation (13.7), equation (13.9) is obtained:

$$N_i = x N_{i-1} (i \geq 2) \tag{13.9}$$

The next step is to obtain the relationship between N_i and N_0. From equation (13.9), N_i can be expressed by N_1 and x as follows:

$$N_i = x N_{i-1} = x(x N_{i-2}) = x^2 (x N_{i-3}) = \cdots\cdots = x^{i-1} N_1 \tag{13.10}$$

Equation (12.1) is transformed as follows:

$$N_1 = \frac{a_1}{b_1} p N_0 \exp\left(\frac{E_1}{RT}\right) \tag{13.11}$$

Then, equation (13.11) is inserted into Equation (13.10):

$$N_i = x^{i-1}\left(\frac{a_1}{b_1}\right) p N_0 \exp\left(\frac{E_1}{RT}\right) = \left(\frac{x^i}{x}\right) p N_0 \exp\left(\frac{E_1}{RT}\right) \tag{13.12}$$

In order to introduce E_L into equation (13.12), equation (13.8) is used:

$$N_i = \frac{a_1}{b_1} g \exp\left(\frac{E_1 - E_L}{RT}\right) x^i N_0 = c x^i N_0 \tag{13.13}$$

where

$$c = \frac{a_1}{b_1} g \exp\left(\frac{E_1 - E_L}{RT}\right) \approx \exp\left(\frac{E_1 - E_L}{RT}\right) \tag{13.14}$$

[Note: Equation (13.14) shows that *c*-constant is always positive.]

The total number of adsorption sites on the solid surface is expressed as N_s, and the total number of adsorbed molecules is given as N_a; thus, the following equations can be derived:

$$N_s = \sum_{i=0}^{\infty} N_i = N_0 + \sum_{i=1}^{\infty} N_i \tag{13.15}$$

$$N_a = \sum_{i=0}^{\infty} i N_i = \sum_{i=1}^{\infty} i N_i \tag{13.16}$$

The next step is to change N_s and N_a into V_m and V_a, the gas volume at the monolayer coverage and the total gas volume adsorbed at the standard state (T=273.15 K and P=101.3 kPa), respectively.

$$\frac{N_a}{N_s} = \frac{V_a}{V_m} \tag{13.17}$$

Inserting Equations (13.15) and (13.16) into equation (13.17), we equation (13.18) can be obtained.

$$\frac{V_a}{V_m} = \frac{\sum_{i=1}^{\infty} iN_i}{N_0 + \sum_{i=1}^{\infty} N_i} \tag{13.18}$$

By using equation (13.13), equation (13.18) can be transformed into Equation (13.19):

$$\frac{V_a}{V_m} = \frac{cN_0 \sum_{i=1}^{\infty} ix^i}{N_0 + cN_0 \sum_{i=1}^{\infty} x^i} \tag{13.19}$$

Equations (13.20) and (13.21) can be derived when x<1.

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} \tag{13.20}$$

$$\sum_{i=1}^{\infty} ix^i = x\frac{d}{dx}\sum_{i=1}^{\infty} x^i = x\frac{d}{dx}\left(\frac{x}{1-x}\right) = \frac{x}{(1-x)^2} \tag{13.21}$$

If equations (13.20) and (13.21) are inserted into equation (13.19), equation (13.22) is obtained:

$$\frac{V_a}{V_m} = \frac{cx}{(1-x)(1-x+cx)} \tag{13.22}$$

where *c* and v_m are constant. Now, consider the physical meaning of x. The experimental fact shows that in the adsorption isotherm, the adsorbed amount, v, becomes infinite at saturation pressure; namely, $v = \infty$ at $p = p_0$. On the other hand, in equation (13.22), v becomes infinite when x is equal to 1. Accordingly, it is concluded that x = 1at $p = p_0$. Inserting these conditions into Equation (13.8), Equation (13.23) is derived:

$$1 = \frac{p_0}{g}\exp\left(\frac{E_L}{RT}\right) \tag{13.23}$$

From equation (13.8) and equation (13.23), the physical meaning of x becomes evident; x is the relative pressure of adsorptive.

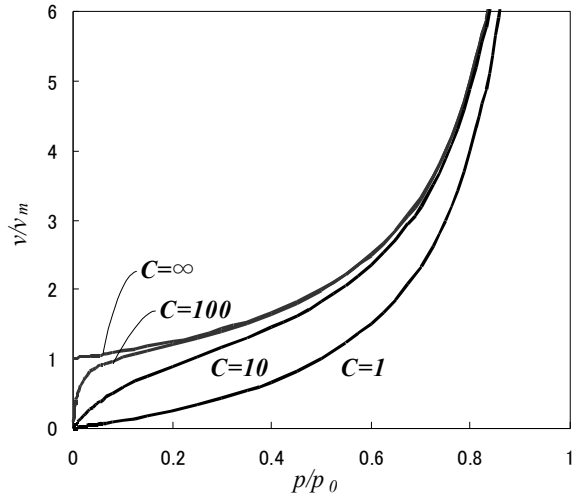
$$x = \frac{p}{p_0} \tag{13.24}$$

If we rewrite equation (13.22) using the relative pressure, equation (13.25) is obtained:

$$V_a = \frac{V_m cp}{(p_0 - p)\left\{1 + (c-1)\left(\frac{p}{p_0}\right)\right\}} \tag{13.25}$$

Equation (13.25) is called the BET equation, or the BET adsorption isotherm. The curves in the above figure show the BET adsorption isotherm at the different c constant. When c is large (*i.e.*, large adsorption heat), the isotherm is of Type II, whereas when c is small (*i.e.*, small adsorption heat), the adsorption isotherm is of Type III.

When c is large and $p \ll p_0$, Equation (13.25) is changed into equation (13.26), which is equivalent to the Langmuir equation.



$$V_a = \frac{V_m c\left(\frac{p}{p_0}\right)}{\left\{1 + c\left(\frac{p}{p_0}\right)\right\}} \qquad (13.26)$$

In order to examine the reliability of the BET equation using the experimental data, equation (13.25) is put into the following form:

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) \qquad (13.27)$$

It is evident from Equation (13.27) that a plot of $(p/V_a(p_0 - p))$ against (p/p_0), which is called the BET plot, should give a straight line, and that the intercept(i) and the slope(s) of the BET plot give $(1/V_m c)$ and $(c-1)/V_m c$, respectively. The two constants $(V_m \text{ and } c)$ of the BET equation can be calculated using Equations (13.28) and (13.29):

$$v_m = \frac{1}{s+i} \qquad (13.28)$$

$$c = \frac{s}{i} + 1 \qquad (13.29)$$

In many adsorbents, the BET plot gives the good linear line in relative pressure range 0.05~0.35, but it deviates from the linear line in low or high pressure range. Usually, V_m and *c* are evaluated from the BET plots in the pressure range of (p/p_0) = 0.05 to 0.35, but the starting point and the ending point of the BET plot should be carefully selected according to the character of adsorbent. For example, in the case of graphitized carbon black (Vulcan 3-G (2700)), the BET plots in the range of 0.040 to 0.145 is recommended in evaluating v_m. In our software, the starting point and the ending point of the BET plot are arbitrarily selected according to the character of adsorbent. V_m can be used in calculation of the specific surface area of adsorbent (a_s) as described below.

Here, some comments are given in the BET equation with three parameters. As mentioned above, the BET plot deviates from the linear line below (p/p_0) = 0.05 and above (p/p_0) = 0.35. Brunauer *et al*. proposed the three parameter equation (Equation (13.30)) in order to cover the wide range of the adsorption isotherm, where n is the number of layer. It is possible to cover the wide range of the adsorption isotherm by selecting an appropriate numerical value of n, but the three parameter equation is not frequently used because of complexity.

$$V_a = \frac{V_m cx}{(1-x)}\left(\frac{1-(n+1)x^n + nx^{n+1}}{1+(c-1)x - cx^{n+1}}\right) \quad (13.30)$$

Equation (13.30) is reduced to Lamgmuir equation (Equation (13.26)) when n = 1.

[Note] There is a criticism that it is inappropriate to apply the BET theory to Type I isotherm. In this case, the maximum value of relative pressure p/p_0 (referred to as BET range limit) is defined as the BET plot end point when relative pressure p/p_0 is plotted on the X axis and Va (p_0-p) is plotted on the Y axis so that C is not a negative value. To determine the starting point, use caution about the following three points: [1] Constant C is not a negative value. [2] Excellent linearity, and [3] Selection of linear range at low relative pressure.

This method is prescribed in ISO9277 appendix. Regardless of the analysis method being used, it must be understood that the target is a gas adsorption surface area, which is different from geometrical surface area.

When C>>1, the BET plot intercept is $1/V_mC$, which is so small that it can be regarded as zero. Thus, the equation (13.27) is expressed as follows:

$$\frac{p}{V_a(p_0-p)} = \frac{C-1}{V_m C}\frac{p}{p_0} \quad (13.31)$$

The following equation is derived by simplifying the equation (28):

$$V_m = V_a\left(1-\frac{p}{p_0}\right) \quad (13.32)$$

Monomolecular adsorption V_m can be obtained by measuring an adsorption amount Va at arbitrary equilibrium pressure p. Thus, V_m can be determined based on measurement of one point at arbitrary equilibrium pressure p (generally, in a relative pressure range of 0.2 to 0.3). (BET1 plot method)

With this analysis software, prepare BET-plot first, and then select one point (end point). By plotting a line between two points (origin (0) and the selected point), the software calculates inclination s of the line, and determines an amount of monomolecular adsorption V_m, and calculates a surface area from the amount of monomolecular adsorption.

It is possible to calculate the total pore volume and mean pore diameter in the analysis, “BET plot”.

To caluculatte the total pore volume, first the amount adsorbed at the relative pressure which can be set in “Analysis parameter” settings is calculated by linear interpolation. Then interporated value, V_p[cm^3 g^{-1}] is converted to the volume liquid state as Equation (13.33). (In case that the relative pressure of last adsorption point is smaller than the set value, the total pore volume is to calculate from amount adsorbed of last adsorption point.)

$$V_p = V / 22414 \times M_g / \rho_a \quad (13.33)$$

where M_g is molecular weight and ρ_a is density of adsorptive. Mean pore diameter can be obtained as follows by using V_p and $a_{s,BET}$, the BET specific surface area.

$$d_p = \frac{4 \times V_p}{a_{S,BET}} \times 10^3 \quad (13.34)$$

Mean particle size is calculated as follows.

$$l = \frac{6}{\rho_S \times a_{S,BET}} \times 10^3 \quad (13.35)$$

where ρ_s is density of adsorbent.

«Reference»

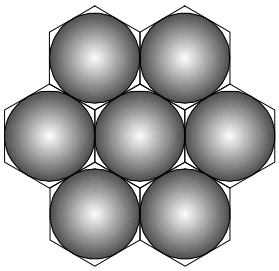
- “Adsorption of Gases in Multimolecular Layers”, Stephen Brunauer, P. H. Emmett and Edward Teller, *J. Amer. Chem. Soc.,* 60, 309(1938).
- ISO9277

13-1-2. Determination of surface area from monolayer volume

Specific surface area of adsorbent (a_s) can be calculated by equation (13.36).

$$a_s = \frac{V_m}{22414} \times L \times \sigma \qquad (13.36)$$

where V_m is monolayer volume, L the Avogadro constant, and σ the cross-sectional area of an adsorbate molecule. σ is defined as the average area that one adsorbed molecule occupies on the solid surface, and it is calculated under the assumption that adsorbed molecules make the closest packing on solid surface. It is obvious from the model shown below that σ corresponds to the hexagonal area, which is evaluated from the molecular weight of adsorbate M and the liquid density of adsorbate ρ.



$$\sigma = 2\sqrt{3}\left(\frac{M}{4\sqrt{2}L\rho}\right)^{2/3} \qquad (13.37)$$

In case of the nitrogen adsorption at liquid nitrogen temperature, $\sigma(N_2)$ = 0.162 nm^2 (M = 28.0, ρ= 0.808 g cm^{-3}) can be calculated from equation (13.35). The cross-sectional area of a nitrogen molecule, which is calculated by a simple model, was checked by the independent methods such as the absolute method of Harkins and Jura. $\sigma(N_2)$ = 0.162 nm^2 is internationally accepted for determination of surface area of many adsorbents. However, it should be mentioned that, when the adsorbed nitrogen molecules have the specific orientation on the unique solid surface, the different value of $\sigma(N_2)$ must be used.

In cases of the Kr or Ar adsorption at liquid nitrogen temperature, σ(Kr, 77 K) = 0.202 nm^2 or σ(Ar, 77 K) = 0.138 nm^2 are estimated from equation (13.35), using the super-cooled liquid density of Kr or Ar.

The cross-sectional areas of various molecules such as alcohols and hydrocarbons are calculated based on $\sigma(N_2)$ = 0.162 nm^2 [*ref.* A. L. McClellan, and H. F. Harnsberger, *J. Colloid Interface Sci.*, **23**, 577(1967).].

13-1-3. Thermodynamics of gas adsorption

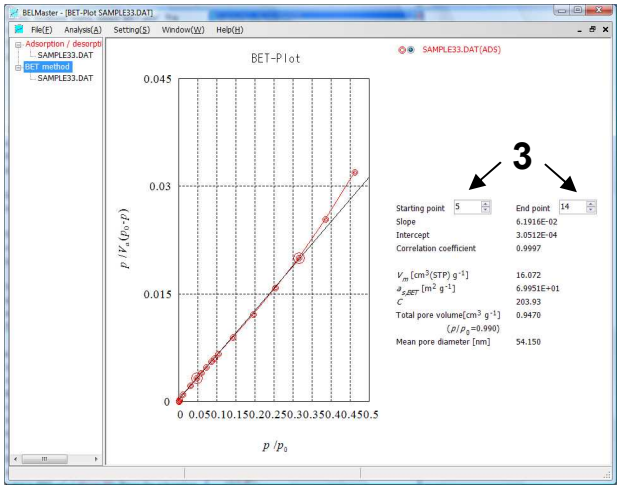
It is well-known that the gas adsorption process is essentially exothermic. The thermodynamic relation of the gas adsorption is given by equation (13.36).

$$\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad} \qquad (13.38)$$

where ΔG_{ad}, ΔH_{ad}, ΔS_{ad} are the Gibbs free energy change of adsorption, the enthalpy change of adsorption, and the entropy change of adsorption, respectively. ΔG_{ad} becomes negative, because the gas adsorption proceeds spontaneously. Furthermore, ΔS_{ad} becomes negative, because the molecules moving at random in gas phase are fixed on the solid surface by adsorption. Accordingly, it is concluded from equation (13.36) that ΔH_{ad} must be negative; namely, the gas adsorption is essentially exothermic.

Operaion

1. On the “Analysis” menu, select “BET plot”. The following BET-plot will be displayed on the screen. The program will execute a BET plot from adsorption data of an isotherm.

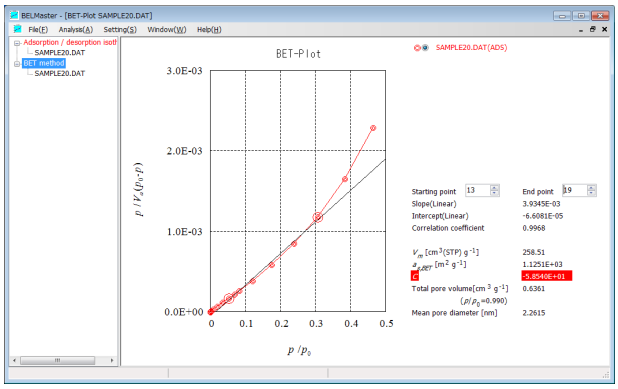


2. The program automatically draws an straight line. As a default, two points are selected that are nearest to the pressure range specified on the “Analysis parameters”.

3. Select the starting and end points in order to produce a good straight line within a relative pressure range of 0.05 to 0.30.

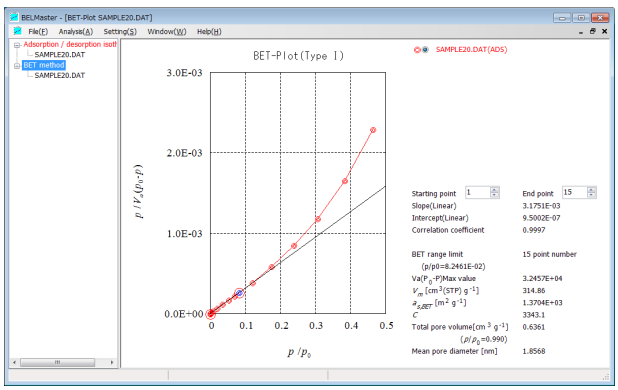
4. The figure on the right is a BET plot of nitrogen adsorption measurements on silica with micropores. The monomolecular adsorption volume (V_m/cm^3 g^{-1}) and C value can be obtained from the slope of the approximate curve and intercept. In addition, the correlation coefficient of this approximate curve is shown.

5. You can obtain a specific surface area ($a_{s,BET}$/m^2 g^{-1}) from the monolayer volume (V_m/cm^3 g^{-1}) for the adsorption of nitrogen, argon, and krypton. In nitrogen adsorption when C is 100 to 200, it is believed that a reliable specific surface area can be obtained. The specific surface area obtained from the BET plot of micropore silica is 70.0 m^2 g^{-1} and this value matches well the value of 70.1 obtained from a t-plot (page 77).



BET-plot of active carbon (p/p$_0$=0.05-0.3)

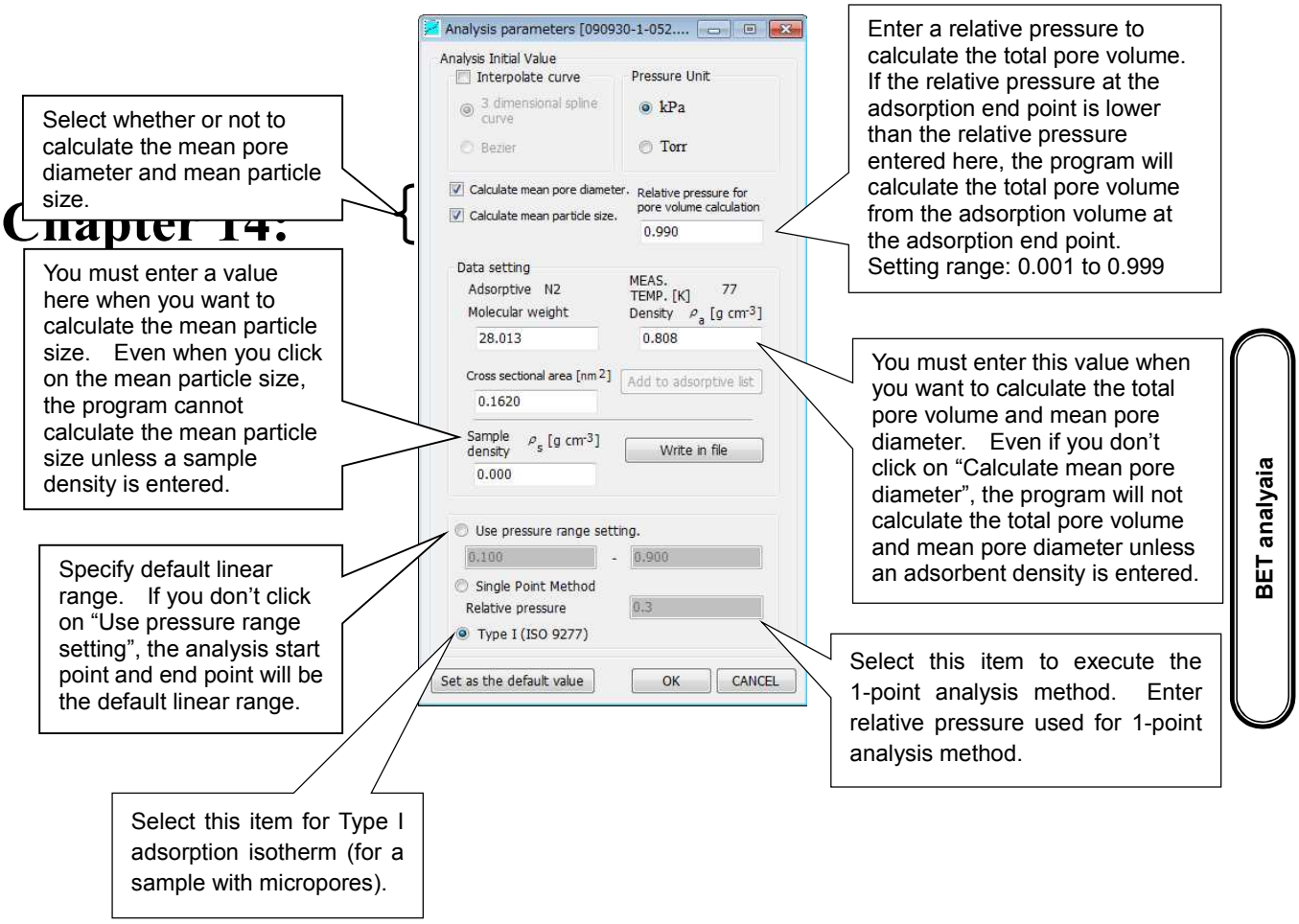
6. The figure on the right is a BET plot for activated carbon.
Regarding nitrogen adsorption on a sample with micropores, C is a negative value (indicated in red) in a relative pressure range of 0.05 to 0.03, which cannot provide a BET-plot with excellent linearity.
In this case, an accurate specific surface area cannot be determined. However, if Type I (ISO9277) is selected in [Analysis parameters], BET specific surface area can be obtained. The specific surface area obtained from the BET-plot of this activated



BET-plot of active carbon (TypeI, ISO9277)

carbon is 1370 $m^2 g^{-1}$. The specific surface area obtained from *t*-plot is 1519 $m^2 g^{-1}$ (p. 80).
Since the amount of adsorption on a micropore surface is larger than that on non-porous surface, the specific surface area obtained from *t*-plot is considered to be larger than the actual area. Therefore, the specific surface area of this activated carbon is estimated at 1400 to 1500. As described above, it is difficult to determine the specific surface area of micropores exactly. However, we can obtain a proper value by using both methods of BET-plot and *t*-plot.

7. Select "Analysis parameters" from the "Settings" menu. The "Analysis parameters" window shown below will appear. Change the settings as needed.

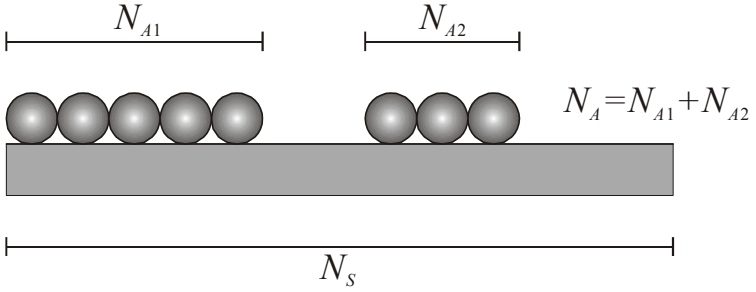


Chapter 14: Langmuir plot

14-1. Description

In 1918, Langmuir proposed the monolayer adsorption theory. He derived the equation for the adsorption isotherm on the following assumption.

1. Adsorption sites on adsorbent surface have the same adsorption energy.
2. One adsorption site is occupied by one adsorbed molecule.
3. There is no lateral interaction between adsorbed molecules.
4. Adsorption is complete when mono-molecular layer (monolayer) is formed.



The Langmuir equation is derived according to the monolayer adsorption model given below. In the model, the whole adsorption sites, the occupied adsorption sites, and the unoccupied adsorption sites on the adsorbent surface are shown as N_S, N_A, and (N_S − N_A), respectively. The surface coverage θ for the occupied adsorption sites is defined as follows:

$$\theta = \frac{N_A}{N_S} \tag{14.1}$$

The adsorption rate, v_a is proportional to p (pressure of adsorptive) and $1-\theta$ (bare surface);

$$v_a = k_a p(1-\theta) \tag{14.2}$$

On the other hand, the desorption rate, v_d is proportional to θ (occupied surface);

$$v_d = k_d \theta \tag{14.3}$$

k_a and k_d in Equations (14.2) and (14.3) are the proportional constants. Under the adsorption equilibrium, the adsorption rate is equal to that of desorption;

$$k_a p(1-\theta) = k_d \theta \tag{14.4}$$

Equation (14.4) is changed into equation (14.5),

$$\theta = \frac{Bp}{1+Bp} \tag{14.5}$$

Where k_a / k_d is shown as B. Furthermore, equation (14.5) is expressed using the monolayer volume, V_m. The amount of adsorbed gas at an arbitrary pressure is expressed as follows;

$$V_a = V_m \theta \tag{14.6}$$

By putting equation (14.6) into Equation (14.5), we obtain equation (14.7), the Langmuir equation.

$$V_a = \frac{V_m Bp}{1+Bp} \tag{14.7}$$

If the condition of $1 \gg Bp$ (low pressure range) is satisfied, equation (14.7) is transformed to equation (14.8);

$$V = V_m Bp \tag{14.8}$$

Equation (14.8) is called Henry equation, where the amount of adsorbed gas is proportional to the adsorptive pressure. Equation (13.7) can be converted to equation (14.9).

$$p/V_a = 1/BV_m + p/V_m \tag{14.9}$$

Equation (14.9) is used to analyze the experimental data. If the adsorption data matches the Langmuir model, the Langmuir plot (p/V_a vs. p) gives a linear line with the slope of $1/V_m$ and the intercept of $1/BV_m$, from which the monolayer volume, V_m and the constant, B can be estimated.

In our software, the Langmuir plot is automatically displayed on the computer screen. Next, if user selects the starting point and the end point, the monolayer volume (V_m), the Langmuir constant (B), and the surface area ($a_{s,Lang}$) can be calculated by means of the least-square method, and are displayed.

[Notice]:

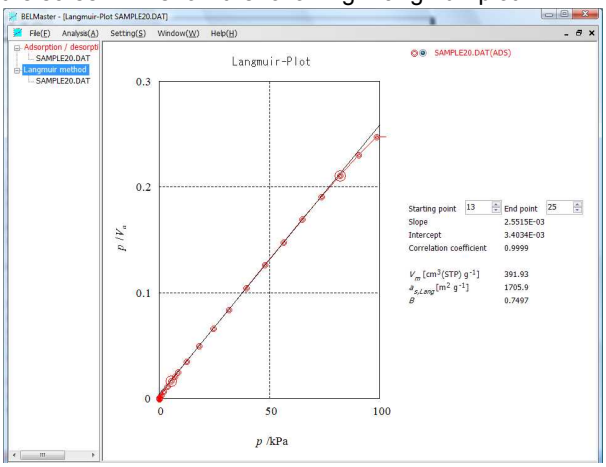
The Langmuir equation (14.7), which is derived from the adsorption model on the nonporous surface (cf. adsorption model given above), gives the Type I isotherm. In the physical adsorption, however, the Type I isotherm is obtained for the microporous adsorbents such as active carbons or zeolites. In such microporous adsorbents, the Type I isotherm can be explained by filling of the adsorbate molecules into micropores; that is, the initial sharp rise of the isotherm corresponds to the filling process of adsorbate into micropores, and the flat region of the isotherm appears when the micropores are completely filled by adsorbate. It is reasonable to conclude that the monolayer volume (V_m) of microporous adsorbent obtained from the Langmuir plot corresponds to the micropore volume. The surface area of microporous adsorbent estimated from V_m occasionally gives the abnormally high value. The surface area of some microporous active carbon, if it is calculated from V_m of the Langmuir plot, reaches 3,000 $m^2 g^{-1}$. This value is larger than the maximum surface area, 2,630 $m^2 g^{-1}$, whose value is estimated by assuming that both sides of the graphite layer in active carbon are covered by monolayer of adsorbate.

«Reference»

- I. Langmuir, *J. Amer. Chem. Soc.* **38**, 2219(1916); **40**, 1368(1918).

14-2. Operation

1. Select “Langmuir plot” from the “Analysis (A)” menu and the screen will show the following “Langmuir-plot” window. The program will execute a Langmuir plot from adsorption data of an isotherm adsorption.



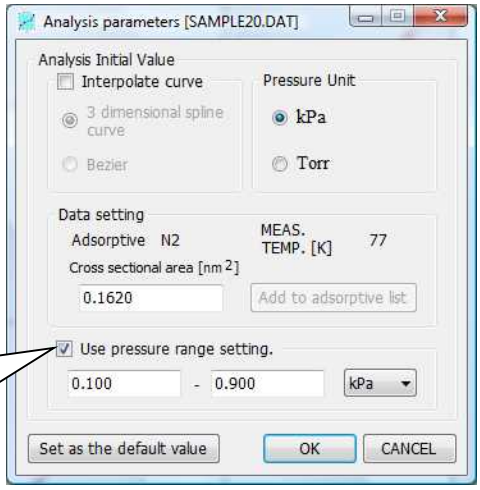
2. The program automatically draws an straight line. The default selection is the start point as the minimum data point and the end point as the maximum data point. The program obtains the monolayer volume (V_m/c m^3 g^{-1}) and the B value from the slope of the approximate curve and intercept. The program will also display the correlation coefficient of the approximate curve.

3. Select the starting and end points to obtain good linearity.

4. In a chemical adsorption volume measurement, the chemical adsorption can be obtained from the monolayer volume (V_m/cm^3 g^{-1}).

5. The nitrogen adsorption isotherm on a sample with micropores is shown as type I, and gives good linearity in a Langmuir-plot. However, as described in the [Description], there is a tendency that the specific area obtained may be larger than the actual value. The figure above shows a Langmuir-plot of microporous activated carbon. The specific surface area obtained will be 1,706 mm^2 g^{-1} and this is larger than the actual value (1,400 to 1,500 m^2 g^{-1}, on page 72).

6. Select “Analysis parameters” on the “Setting” menu. The “Analysis parameters” window shown below will appear. Change the settings as needed. For details about items not described here, see section 7-1 ”Analysis parameters,” on page 37.



Enter a default linear range. If you do not click on “Use pressure range setting”, the analysis start point and end point will be the default linear range. The pressure unit can be set to either kPa or Toor.

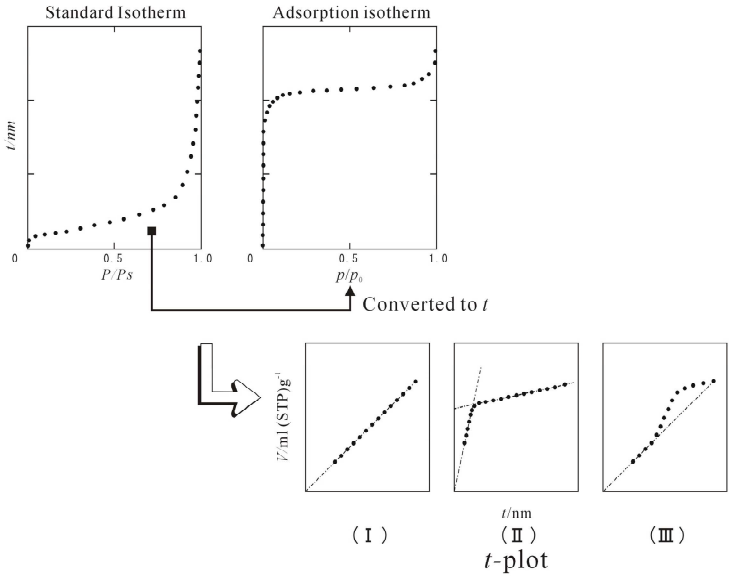
Chapter 15: t plot

15-1. Description

Adsorption amount depends on gas pressure, adsorption temperature, and properties of adsorptive gas and adsorbent solid. In a nitrogen adsorption isotherm measurement, temperature is constant and gas is limited, thus the isotherm changes according to the property of solid. However, in case of non-porous solid, although there is difference in adsorption amount, there is almost no difference in the shape of isotherm. In this case, plural isotherms can be expressed in one isotherm by standardizing adsorption amount. This is the concept of standard isotherm. There are many ways of standardization, but the one that was suggested by Shull et al. is frequently used. In this method, adsorption amount is expressed by the thickness of adsorption layer *t,* and the equation is as follows:

$$t = \frac{V_a}{V_m} \times 0.354[\mathrm{nm}] \qquad (15.1)$$

0.354 nm is the thickness of monomolecular layer. This value is obtained with a hypothesis that nitrogen molecules make hexagonal closest packing on adsorbent surface; therefore, it is smaller than the diameter of nitrogen molecule. Standard t-curve can be calculated from (15.1) converting adsorption isotherm of vertical axis (adsorption amount) to thickness of adsorption layer.



The t-plot method, which was invented by Lippens and de Boer, compares the above-mentioned standard isotherm and arbitrary isotherm. Standard isotherm shows the relationship between relative pressure and thickness of adsorption layer. Using standard isotherm, x-axis of isotherm that you wish to analyze can be changed from relative pressure to thickness of adsorption layer. Obtained t-plot can be divided into 3 types in broad term (Above diagram).

(3 different types of t-plot from (I) to (III) are shown above, but this categorization is just for the matter of convenience, and there is no type defined by IUPAC like in adsorption isotherm.)

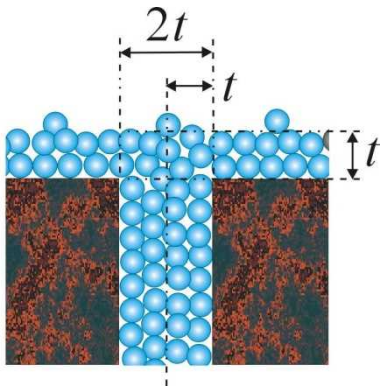
If t-plot is a linear curve that passes the original point like (I), it means that adsorption amount increased at the same rate as standard isotherm, and thus the adsorbent is considered to be non-porous material. Here, the increased adsorption amount when adsorption layer increases by one layer (*t*=0.354nm) is equal to

mono-molecular adsorption amount. Therefore, specific surface area a_s[m^2 g^{-1}] can be calculated from the following equation with the slope of t-plot, *s*.

$$a_s = \frac{s \times 0.354}{22414} \times L \times \sigma = 1.541 \times s \qquad (15.2)$$

Here, *L* is Avogadro constant and *σ* is cross sectional area of adsorptive.

If t-plot has 2 different slopes like (II) that one of them is a sharp slope passing the original point and the other is more gradual slope, it means that the adsorbent has homogenious sized micropores. In the early stage of adsorption, adsorption amount increases drastically due to adsorption into micropores (micropore filling) but the thickness of adsorption does not increase so much, as the result, the slope of t-plot becomes sharp. When adsorption into micropores is completed, adsorption happens only on the surface. As a result, the slope of the curve becomes gradual. At this point, whole surface area (a_1) can be calculated by applying the slope of the linear curve L1 to equation (15.1). In the same manner, external surface area (a_2) can be calculated by applying the slope of the other curve L2 to the equation. Pore surface area can be calculated by subtracting a_2 from a_1. Pore volume can be obtained by converting the value of Y intercept of L2 to a volume under liquid condition. Furthermore, adsorption condition is considered to be like in the figure above at intersecting point of L1 and L2. Thus, doubled value of *t* (value 2*t*) is regarded as the average pore diameter. However, value 2*t* gives wrong analysis results when pore size is only 2 layer or less. When 2*t* value is smaller than 0.7nm, as it is micropore filing you can have rough idea whether the pores are big or small but there is no credibility in terms of numerical value.



If t-plot draws a sharp straight line which begins from the original point but becomes smoother curve from some point like (III), the adsorbent is considered to have mesopores. The deviation from the linear curve is due to capillary condensation. Even in t-plot of this type, whole surface area can be measured from linear that passes the original point like in case of (I).

Standard isotherm was invented originally with a purpose to express all the type II isotherms by one conversion isotherm. However, as research progressed it was found that one standard isotherm was not enough. Therefore, BEL Japan software contains 6 standard isotherms (4 of them are calculated from adsorption isotherm on non-porous material, and 2 of them are from the literature). It is ideally best to produce standard isotherm with non-porous material which surface chemical property is same as the sample to be analyzed. But it is difficult to produce such standard isotherm in a practical sense. For this reason, Brunauer et al. divided the statistical t-curves into categories by C-constant of BET method, and suggested that it is better to select one that has similar C-constant to the isotherm of the analyzed sample. C-constant is certainly a factor that indicates interaction between adsorptive and adsorbent, and it depends on not only by chemical property but also by porous structure. When micropores exist, C-constant becomes very large and standard isotherm cannot be selected with this value. BEL Japan recommends choosing standard isotherm of a material that has similar to your sample in terms of bulk property.

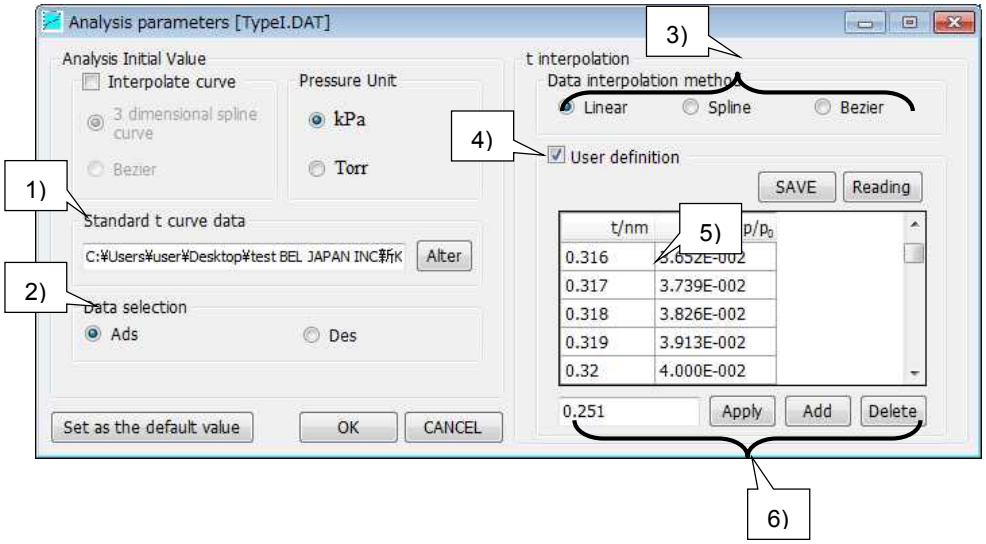
«Reference»

- "Studies on Pore Systems in Catalysts V. The *t* Method", B. C. Lippens and J. H. de Boer, *J. Catalysis,* 4, 319 (1965).

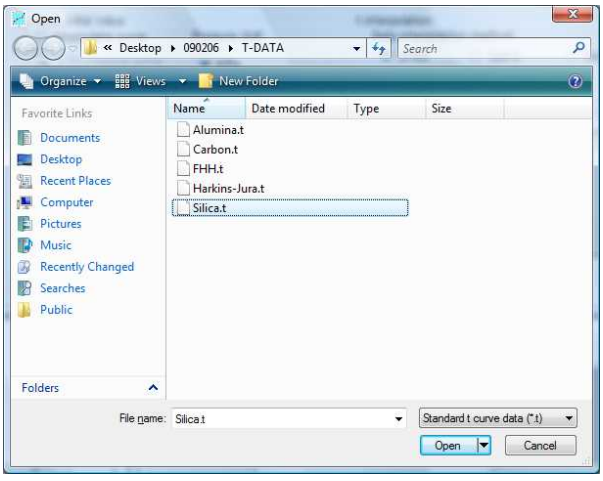
15-2. Operation

1. Select “t-plot” on the “Analysis (A)” menu and the screen will show the following t-plot windows. The program will execute t -plot calculations from the adsorption data of a nitrogen isotherm.

2. Select “Analysis parameters” on the “Setting” menu. The “Analysis parameters” window shown below will appear. Change the settings as needed. For details about items not described here, see section 7-1. “Analysis parameters,” on page 37.



1) Select a standard t-curve.
   - Select a standard isotherm that has similar chemical characteristics to the sample surface.
   - Click on the [Alter] button and the following selection window will appear. Select a set of standard t-curve data file and click on [Open].

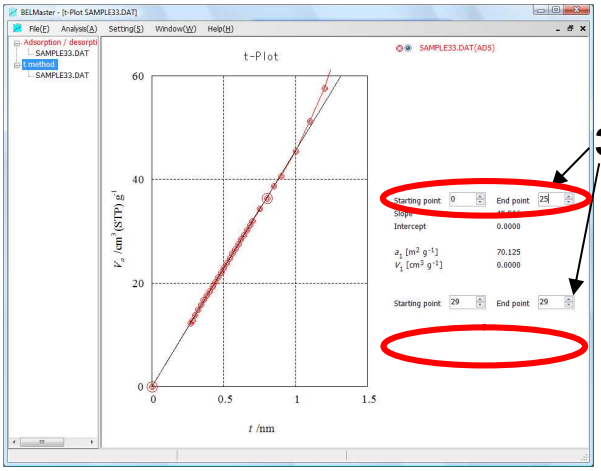


2) Select which data will be used for calculation, the adsorption branch or desorption branch.
3) Select an interpolation method for the file data.
   - You can set the interpolation method to Linear, Spline or Bezier.
4) If interpolation method is not selected, the program will calculate a t-plot at the default setting point. When any method is selected, the program will calculate the t-value specified in the table below.

4) t-data setting.
   - This table can be edited when you click on “User definition”.
5) Edit t-data settings.
   - Click on the [Apply] button and the selected cell (yellow) data will be overwritten with the value displayed in the box.
   - Click on the [Add] button the data displayed in the box will be added.
   - The data that is applied or added are automatically sorted from top to bottom.
   - Click on the [Delete] button and the selected data will be deleted.

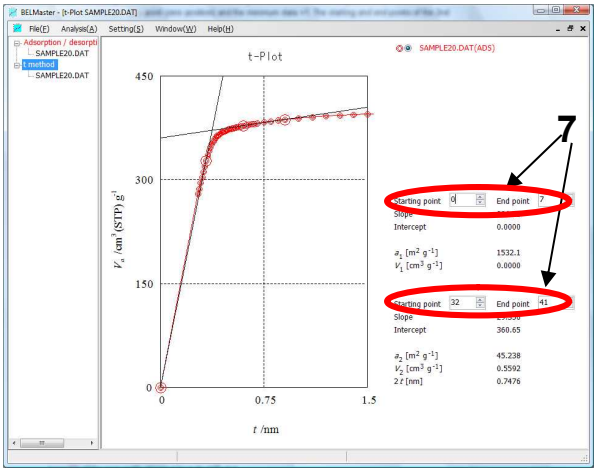
3. In a t-plot, the program will automatically draw two straight lines. The default starting and end points of the 1st line are the minimum data point (zero position) and the minimum data +1. The starting and end points of the 2nd line are the maximum data point -1 and the maximum data point.

4. The figure on the right is a t-plot of a nitrogen isotherm for macroporous silica. “silica-BET.t” is used as a standard isotherm. When selecting a standard isotherm whose chemical characteristics are similar to the sample surface, a good linear t-plot can be obtained that passes through the zero position.



5. Select a start point (normally the zero position) and an end point for the first straight line. From the slope of this line, a specific surface area (a_1) 70.1 m^2 g^{-1} is calculated. This value is a good match for the 70.0 m^2 g^{-1} obtained from the BET plot (page 72). The 2nd straight line is not needed. Set the the starting and end points as the same point and delete the line.

6. The figure on the right is a t-plot of a nitrogen isotherm for microporous activated carbon. “NGCB-BET.t” was specified as the standard isotherm.

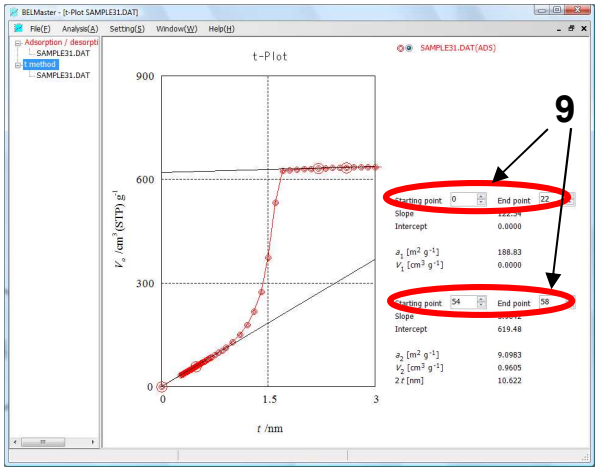


7. Select a starting point (normally the zero position) and end point of the first straight line. The program will calculate the specific surface area (a_1) 1,532 m^2 g^{-1} from the slope of this straight line. Select the starting and end points of the 2nd line. Using the slope of this straight line, the external surface area (a_2) 45 m^2 g^{-1} can be obtained. The volume (V_2) of micropores 0.559 cm^3 g^{-1} can be calculated from the intercept. A micropore area of 1,474 m^2 g^{-1} is obtained from a_1 and a_2 (a_1- a_2). Also, if there is an apparent deflection by completed filling adsorbate into micropores, the pore diameter (2t/nm) can be obtained from the crossing point of the two straight lines.

   The pore diameter of activated carbon is 0.75 mm and this value is a good match for the peak value (0.8 nm

on page 90) of the pore width obtained from the MP-plot.

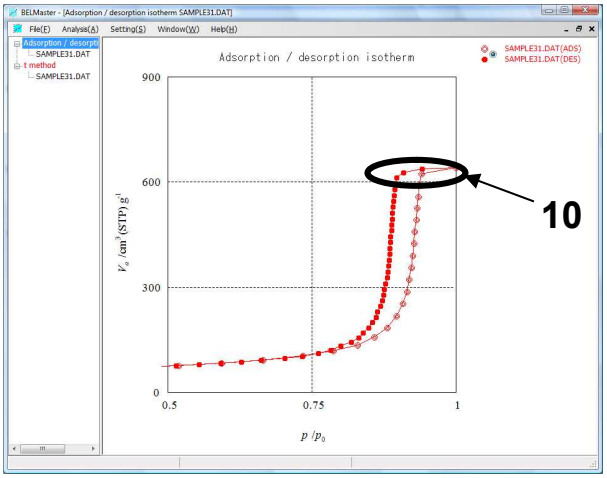
8. The figure on the right is a t-plot of a nitrogen isotherm for mesoporous silica. “silica-BET.t” is used as a standard isotherm. The “User definition” was clicked on and the calculation range was widened to 3 nm.



9. Select a starting point (normally the zero position) and an end point of the 1st straight line. The program will calculate the specific area (a_1) as 189 m^2 g^{-1} from the slope of this line.

10. If the adsorption volume is saturated (figure on the right) in an adsorption/desorption isotherm, it may be assumed that the adsorbate (nitrogen) filling all of the pores is completed. In this case, select starting and end points for the 2nd straight line. The external surface area (a_2) 9 cm^3 g^{-1}can be obtained from the slope of this line and the mesopore volume (V_2) 0.965 cm^3 g^{-1} is calculated from the intercept.

The mesopore area can be obtained as 180 m^2 g^{-1}, from a_1-a_2.



Chapter 16: α_s plot

16-1. Description

Like *t* analysis, α_s method calculates specific surface area of sample by comparing isotherm of standard sample and isotherm of the sample.

t value, which is calculated from standard isotherm and is used in *t* method analysis, indicates the thickness of adsorption layer, but the reliability of the numerical value will be lost when 2*t* is below 0.7.

$$t = \frac{V_a}{V_m} \times 0.354[\mathrm{nm}] \qquad (16.1)$$

t value was originally invented to calculate the thickness of adsorption layer on the pore wall when pore size distribution is drawn from IV type isotherm. When only comparison with the isotherm of standard sample is intended, values of adsorption layer thickness and monolayer capacity V_m are not necessary. Also, when single molecular layer is not formed or when BET-plot does not come into effect, monolayer capacity cannot be calculated and it is impossible to use *t* analysis.

In order to solve the problem of *t* method analysis, Sing et al. (1968) suggested α_s method, which analysis is carried out by standardization with $n_{0.4}$ (adsorption amount at relative pressure, p/p_0=0.4, of N2 adsorption isotherm at 77K of standard sample) rather than by standardization with *t* value. [1)2)]

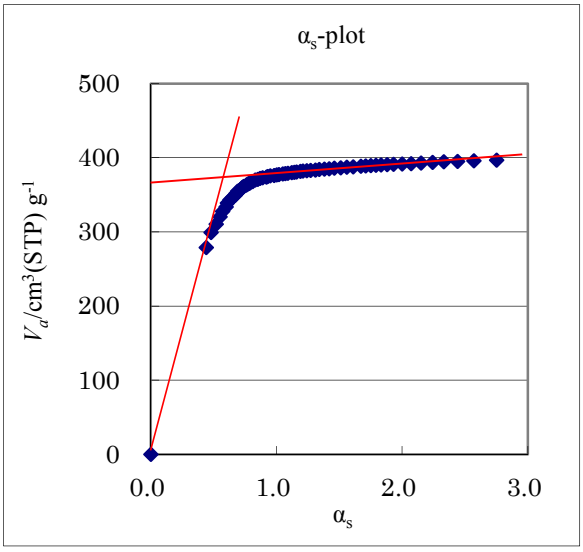
$$\alpha_s = \frac{n_a}{n_{0.4}} \qquad (16.2)$$

n_a indicates adsorption amount at arbitrary equilibrium pressure.

The reason that relative pressure for standardization was set to 0.4 is due to the following reasons:

1. Interaction behavior between adsorbent and adsorbate appears on isotherm below this relative pressure.
2. It is theoretically proved that hysteresis closes at p/p_0=0.42.

The actual analysis procedure is that α_s value of standard sample is calculated from (16.2), and thenα_s curve is drawn (=α_s against p/p_0). The p/p_0 value of an isotherm can be converted to α_s value by using α_s-curve and α_s-plot can be drawn.



Analysis process is basically same for α_s-plot and *t*-plot. Like in *t*-plot, there are 3 different types of α_s-plot and specific surface area can be calculated from the linear curve slope. The slope of α_s-plot of standard sample is calculated, which is $b_{\alpha(\mathrm{standard})}$. Also, the slope of the first linear curve is calculated from α_s-plot of analysis sample, which is $b_{\alpha(\mathrm{test})}$.

The ratio between the above mentioned $b_{\alpha(\mathrm{standard})}$ and $b_{\alpha(\mathrm{test})}$ is equal to the ratio between two specific surface areas. Therefore, if standard sample specific surface area is expressed by $a_{s(\mathrm{standard})}$ and sample specific surface area is expressed by $a_{s(\mathrm{test})}$,

$$\frac{b_\alpha(test)}{b_\alpha(standard)} = \frac{n_{0.4}(test)}{n_{0.4}(standard)} = \frac{a_s(test)}{a_s(standard)} \quad (16.3)$$

thus

$$a_s(\text{test}) = \frac{b_\alpha(\text{test})}{b_\alpha(\text{standard})} \times a_s(\text{standard}) \quad (16.4)$$

$b_{\alpha(\text{standard})}$ and $a_{s(\text{standard})}$ are already known in this case, thus

$$k = \frac{a_s(\text{standard})}{b_\alpha(\text{standard})} \quad (16.5)$$

$$a_s(\text{test}) = b_\alpha(\text{test}) \times k \quad (16.6)$$

Whole specific surface area a_1 [$m^2\ g^{-1}$] of the sample can be calculated with (16.6).

External surface area a_2 [$m^2\ g^{-1}$] and pore volume V_p[$cm^3\ g^{-1}$] can be calculated from the slope of the second linear curve and the intercept respectively. Moreover, internal surface area of pore can be calculated by subtracting external surface area a_2 from Whole specific surface area a_1 (Refer to Chapter 15 t-method analysis).

Unlike *t* method analysis, in α_s-analysis, the average pore radius cannot be worked out from the intersecting point of the 2 linear curves that are obtained from the plot. However, it is possible to calculate pore radius by hypothesizing the shape of pore as slit shape or cylinder-shape.

e.g.: in case of cylinder-shaped pore (pore radius=*r*, pore length=*L*)

Inside volume of pore(V_p)=pore volume $V_p=\pi r^2 L$ [1]

Internal surface area of pore(a_i)=whole surface area - external surface area $a_i = a_1 - a_2 = 2\pi rL$ [2]

From [1] and [2], pore radius is calculated as follows.

$$r = \frac{2V_p}{a_i} = \frac{2V_p}{a_1 - a_2} \quad [3]$$

In *t* method analysis, it is impossible to evaluate pore size below 3.5nm because there would be no physical meaning when *t* value is below 0.35nm. However, there is no dimension in α_s-value, thus it is possible to compare adsorption interaction at low relative pressure. In α_s-plot, the first linear curve can be drawn easily because plot can be obtained even when α_s-value is small. Also, the first linear curve has to pass the original point in t method analysis, but in α_s-analysis it is possible to select the range without the fixed original point so that linear curve can be drawn easily.

It is suggested that non-porous material that has similar surface to the sample analyzed should be chosen for the standard isotherm (sample for comparison). BEL Japan analysis software contains standard isotherms that are made from N_2 adsorption on non-porous material of SiO_2, Al_2O_3 and Carbon (Graphitized Carbon and non Graphitized Carbon). Select a most suitable standard isotherm to your sample.

Furthermore in α_s-method, there is an advantage that it can be used with other adsorbate other than nitrogen because it does not need the values of monomolecular layer adsorption amount or adsorption cross-section area of adsorptive.

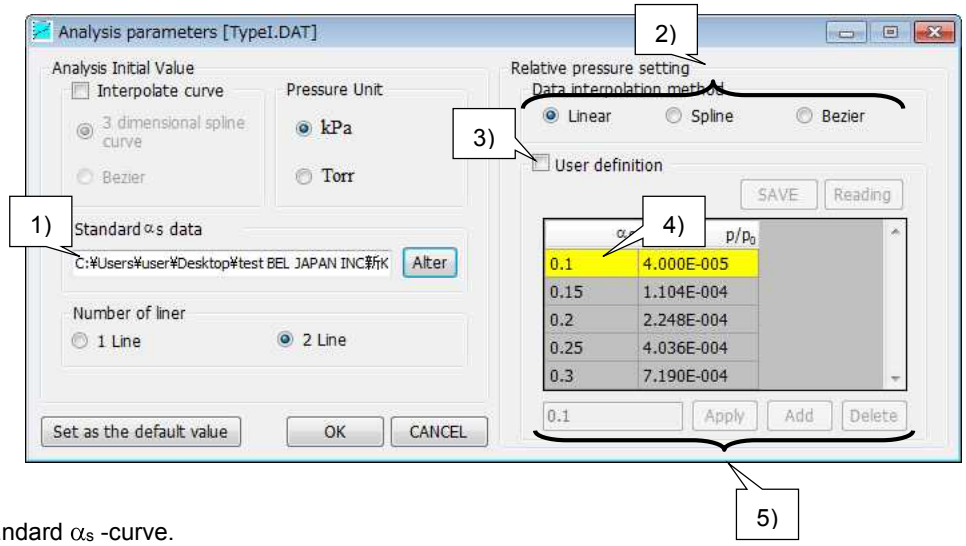
«Reference»

1) D.Atkinson, A.I.McLeod, K.S.W.Sing, *J.Chim.Phys*., **81**,791(1984)
2) K.S.W.Sing, *Carbon*, **27**,5(1989)

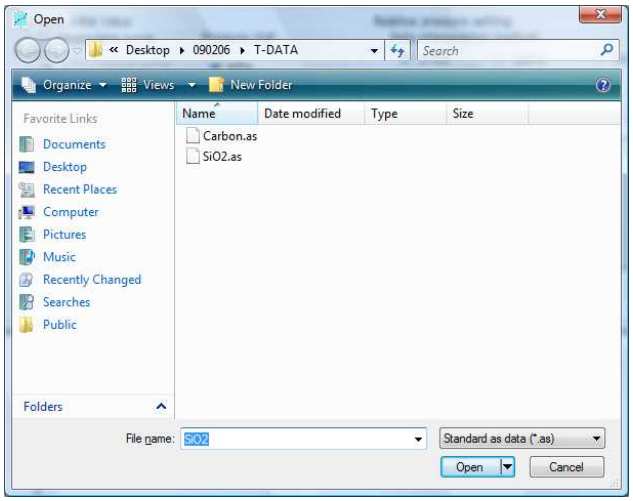
16-2. Operation

1. Select “αs plot,” on the “Analysis (A)” menu and the screen will show the following αs plot windows. The program will execute an αs plot from adsorption data of an isotherm.

2. Select “Analysis parameters” on the “Setting” menu. The “Analysis parameters” window shown below will appear. Change the settings as needed. For details about items not described here, see section 7-1. “Analysis parameters,” on page 37.



1) Select a standard αs -curve.
   - Select a standard isotherm that has similar chemical characteristics to the sample surface.
   - Click on the [Alter] button. The following selection window will appear. Select a standard αs -curve file and click on the [Open] button.

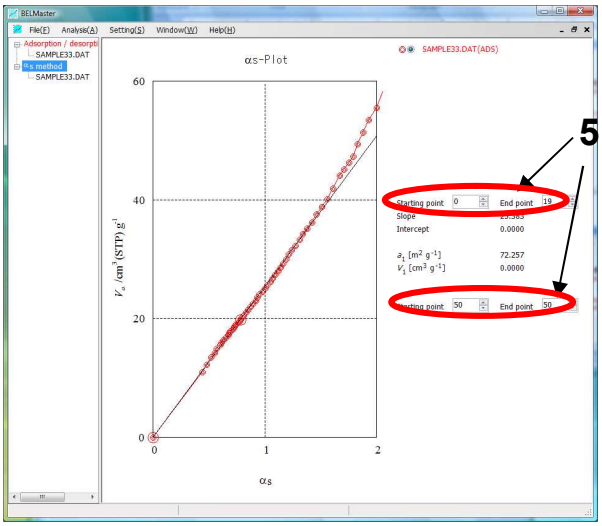


2) Select a method for interpolating the file data.
   - You can select Linear, Spline or Bezier.
3) If “User defintion” is not clicked, the program will calculate an αs -plot at the default setting point. When you click on “User definition”, the program will calculate the αs value specified in the table below.
4) αs setting
   - When “User definition” is selected, this table can be edited.
5) Edit the αs setting.
   - Click on the [Apply] button. The selected cell (yellow) data will be overwritten by the value displayed in the

box.

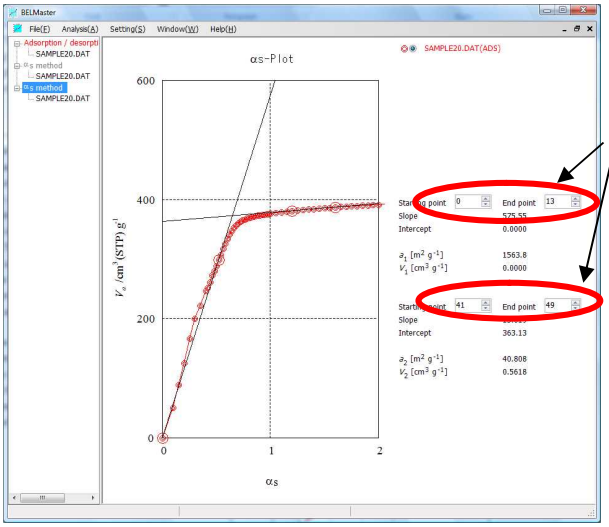
- Click on the [Add] button. The data displayed in the box will be added.
- The modified and added data are sorted automatically in top to bottom order.
- Click on the [Delete] button and the selected data will be deleted.

3. In an α_s -plot, the program automatically draws two straight lines. As a default, the starting and end points of the 1st line are the zero position and the first point, and the starting and end points of the 2nd line are the maximum data point -1 and the maximum data point.



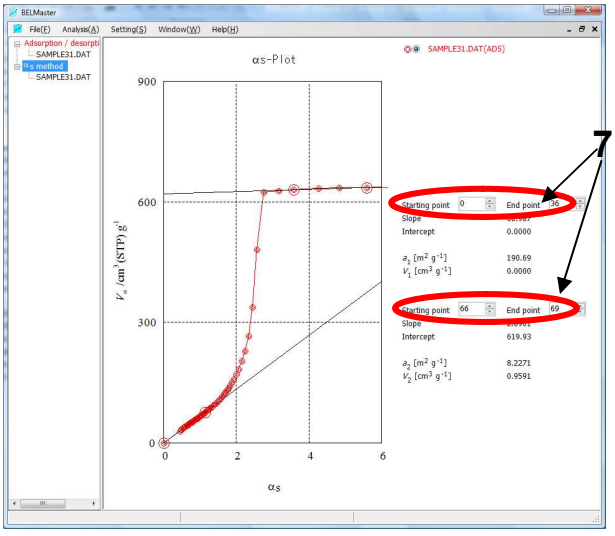
4. The figure on the right is an α_s -plot of a nitrogen adsorption isotherm for macroporous silica. “SiO2.as” is used as a standard isotherm. When selecting a standard isotherm whose chemical characteristics are similar to the sample surface, good linearity can be obtained as the α_s -plot passes through the zero position.

5. Select a starting point (normally the zero position) and end point of the first straight line. The specific area (a_1) 72.3 m^2 g^{-1} is calculated from the slope of this line. The 2nd straight line is not needed. Use the same point as both the starting and end points and delete the straight line.



6. The figure on the right is an α_s -plot of a nitrogen adsorption isotherm for microporous activated carbon. “NGCB-BEL.as” is specified as the standard isotherm. Select a starting point (normally the zero position) and end point of first the straight line. From the slope of this straight line, the program will calculate the specific area (a_1) 1,564 m^2 g^{-1}. Select the starting and end points of the 2nd line. The external surface area (a_2) 41 m^2 g^{-1} can be obtained using the slope of this straight line. The volume (V_2) of the micropores 0.562 cm^3 g^{-1}can be calculated from the intercept. The pore area of the micropores is obtained as 1,523 m^2 g^{-1}, from (a_1 - a_2).

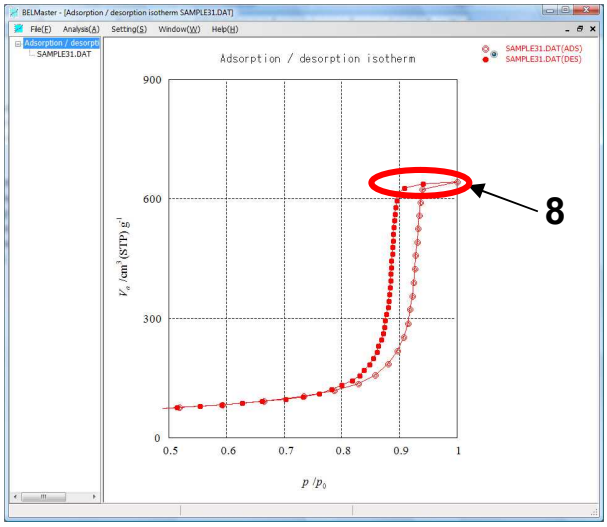
7. The figure on the right is an α_s -plot of nitrogen adsorption isotherm for mesoporous silica. “silica-BEL.as” is used as a standard isotherm. Select a starting point (normally the zero position) and an end point for the 1st straight line. The program will calculate the specific area (a_1) 191 m^2 g^{-1} from the slope of this line.



αs plot

Analysis of measured data

8. In an adsorption/desorption isotherm, if the adsorption volume is saturated (figure on the right), it may be assumed that the adsorbent (nitrogen) has filled all the pores.



9. Select the starting and end points of the 2nd straight line. From the slope of this line, the external surface area (a_2) 8.2 m^2g^{-1} can be obtained. The mesopore volume (V_2) 0.96 cm^3 $g^{-1}$is calculated from the intercept. The area of the mesopores can be obtained as 182 m^2 g^{-1}, from (a_1 - a_2).

αs plot

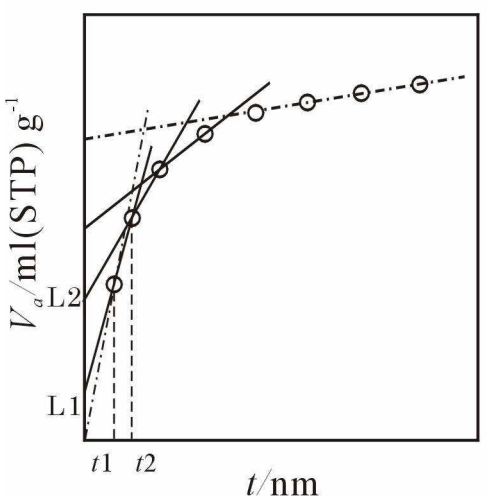
Chapter 17: MP method analysis

17-1. Description

In case of samples with micropores, the slope of t-plot decreases at a certain point (refer to Chapter 15 t-method analysis). If the size of micropores is homogenous, the plot will be on either of the two lines. In other words, the straight line from the origin should be bent sharply at the point when filling into micropores is complete. However, plots have curvature. This means that there is distribution in pore size. In short, MP method measures distribution from the curvature of t-plot. In order to perform MP method analysis, t-plot has to be produced first.

The slope ($s2$) of the linear curve (L2), which connects the 1st point and the 2nd point, is smaller than the slope ($s1$) of the linear curve (L1), which connects original point and the 1st point. This is because pores are filled with adsorbate. The surface area of pore can be expressed by the difference between a_1 and a_2, which are both calculated by multiplying each slope by 1.541. Pore volume V_1 [ml·g-1] can be calculated by multiplying a_1 by thickness of adsorption layer. Thickness of adsorption layer used in this method is the average value of the thickness of 1st and 2nd layer (t_1 and t_2 respectively), so the following equation can be made.

$$V_1 = (a_1 - a_2) \times (t1 + t2) / 2 \times 10^{-3} \qquad (17.1)$$



Distribution curve can be obtained by carrying out the same calculation until the end point of t-plot and then plotting the obtained pore volume against the thickness of adsorption layer (average value). a_1 in MP method is the surface area that is calculated from linear curve that passes the original point, and a_2 is the one that is calculated from the other linear curve. V_p is an integrated value of pore volume, which can be obtained in (17.1). Although d_{peak} is the peak position it is not suitable for MP method analysis when d_{peak} is below 0.7 nm, due to the same reason for the fact that average pore diameter is not accurate unless 2 or more adsorption layers are formed in pores.

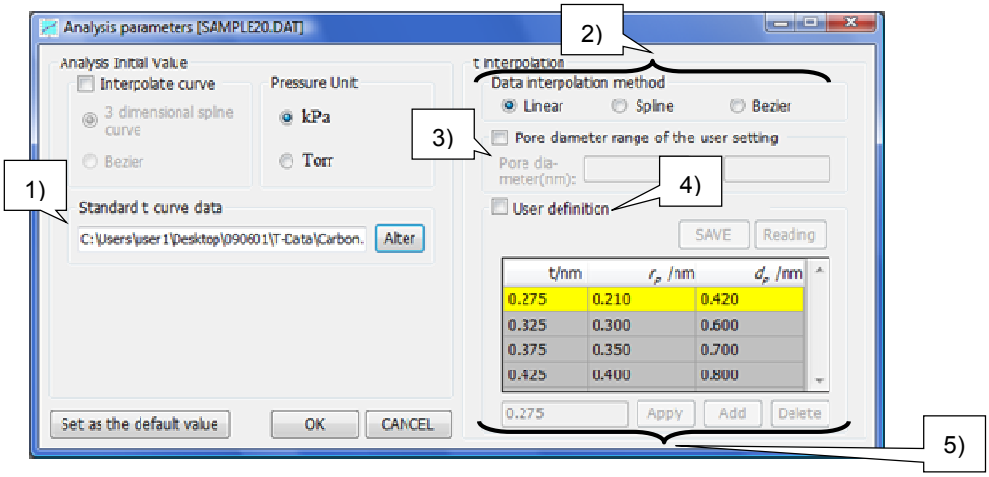
«Reference»

- "Investigations of a Complete Pore Structure Analysis I. Analysis of Microstructure", R. Sh. Mikhail, Stephen Brunauer, and E. E. Bodor, *J. Colloid Interface Sci.,* 26, 45 (1968).

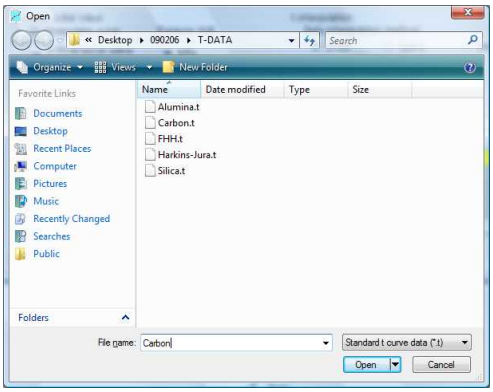
17-2. Operation

1. Select “MP plot” on the “Analysis (A)” menu. The screen will show the following MP plot windows. The program will execute an MP plot from adsorption data of a nitrogen isotherm.

2. Select “Analysis parameters” in the “Setting” menu. The “Analysis parameters” window shown below will appear. Change the settings as needed. For details about items not described here, see section 7-1. “Analysis parameters,” on page 37.

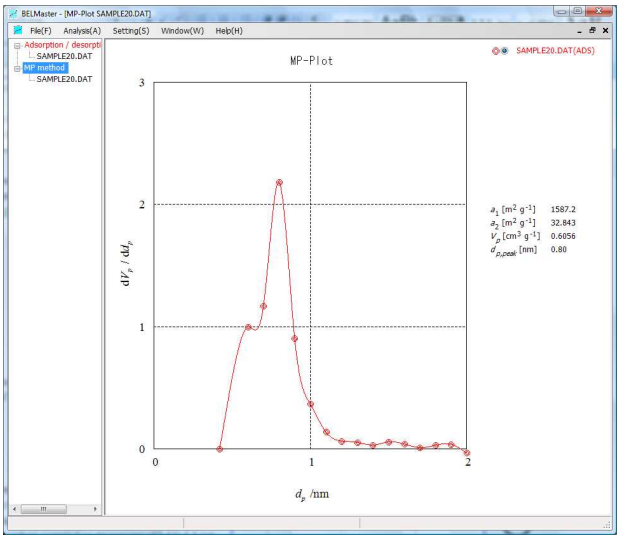


1) Select a standard t-curve.
   - Select a standard isotherm that has similar chemical characteristics to the sample surface.
   - Click on the [Alter] button and the following selection window will appear. Select a standard t-curve data file and click on the [Open] button.

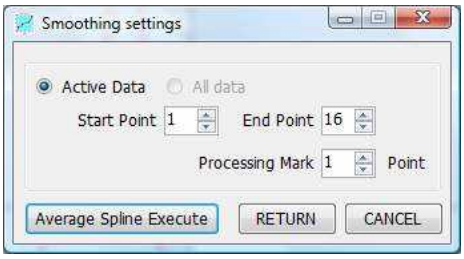


2) Select an interpolation method for the file data.
   - You can select Linear, Spline or Bezier.
3) If “Pore diameter range of the user setting” is not selected, the program will calculate using the default range. When “Pore diameter range of the user setting” is selected, the program will calculate the pore diameter range specified in the table below.
4) If “User definition” is not selected, the program will calculate a t-plot using the default setting point. When “User definition” is selected, the program will calculate the t value specified in the table below.
   t value settings
   - When the “User definition” is selected, this table can be edited.
   - Click on the [Apply] button and the selected cell (yellow) data will be overwritten by the value displayed in the box.

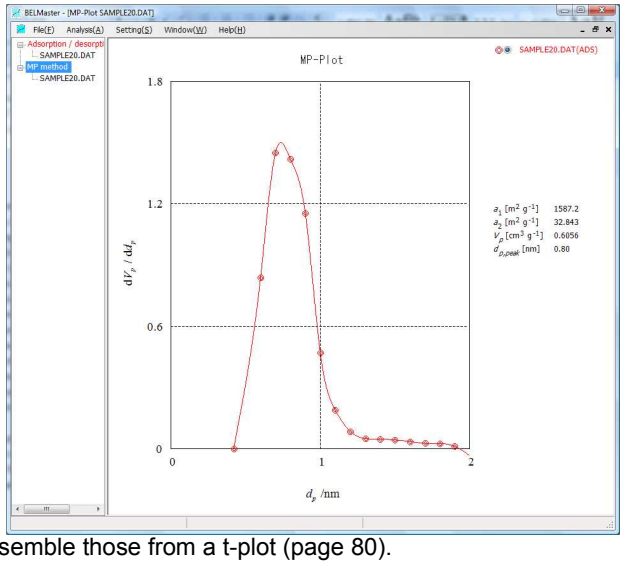
- Click on the [Add] button and the data displayed in the box will be added.
- The modified and added data are automatically sorted in order from top to bottom.
- Click on the [Delete] button and the selected data will be deleted.



3. The figure on the right is an MP-plot of a nitrogen adsorption measurement on microporous activated carbon. "NGCB-BEL.t" is used as a standard isotherm.



4. When you want to smooth the lines, select "Smoothing settings" on the "Settings" menu. The "Smoothing settings" window shown on the right will appear.



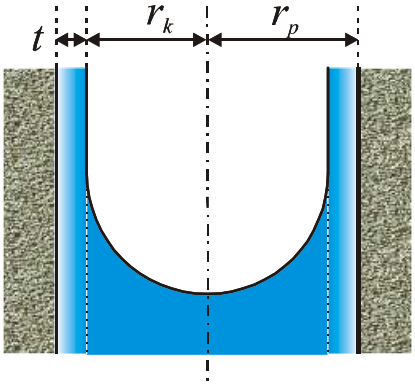
5. The figure on the right shows the result of clicking on the [Average Spline Execute] button to perform one round of smoothing. It can be seen from the figure that this activated carbon sample has micropores of 0.4 to 1.1 nm diameter (d_p), and has a distribution peak ($d_{p,peak}$/nm) at 0.8 nm. From the slope of the 1st straight line that passes the t-plot zero position, the program will calculate the total specific surface area (a_1/m^2 g^{-1}). From the slope of the last straight line, the program will calculate the external specific surface area (a_2/m^2 g^{-1}). Further, by multiplying the product of the surface area at each point by the thickness of the adsorption layer, the pore volume (V_p/cm^3 g^{-1}) can be obtained. Since the MP-plot is an analysis method derived from a t-plot, the results of the MP-plot closely resemble those from a t-plot (page 80).

6. The MP-plot is greatly influenced by the difference in chemical characteristics between a sample surface and a standard material, and by the micropore filling effect, so it will not produce a smooth curve. However, the MP-plot is useful for determining the existence or absence of micropores and their range of size. Please note that even when there are no micropores, the MP-plot will analyze a sample as though there is a peak micropore area.

Chapter 18: BJH plot

18-1. Description

In type IV adsorption isotherms, hysteresis occurs in adsorption and desorption processes. The hysteresis shape depends on the shape of mesopore. Whenever hysteresis exists, equilibrium adsorption amount at desorption is larger than the one at adsorption. This is because capillary condensation of nitrogen gas happens in mesopore and there is difference in meniscus between in adsorption process and in desorption process. There is an equation which represents the relationship between mesopore size and critical condensation pressure, Kelvin equation, and some analysis using Kelvin equation to calculate pore size distriburtion have been reported. Some of these methods are based on the assumption that the mesopores have cylinder shape (Dollimore & Heal method, Cranston & Inkley method and etc.). Pore size distribution is calculatied from desorption isotherm. In 1951, Barrett, Joyner and Halenda proposed a method to evaluate pore size distribution. Pore curve is expressed as percentage change of pore volume($\Delta V_p/\Delta r_p$) against micropore radius(r_p).



In the area where capillary condensation is in presence, radius of cyrinder shaped pore is sum of the thickness of adsorption layer at the arbitrary pressure (*t*) and core radius (r^k) of meniscus part.

$$r_p = t + r_k \tag{18.1}$$

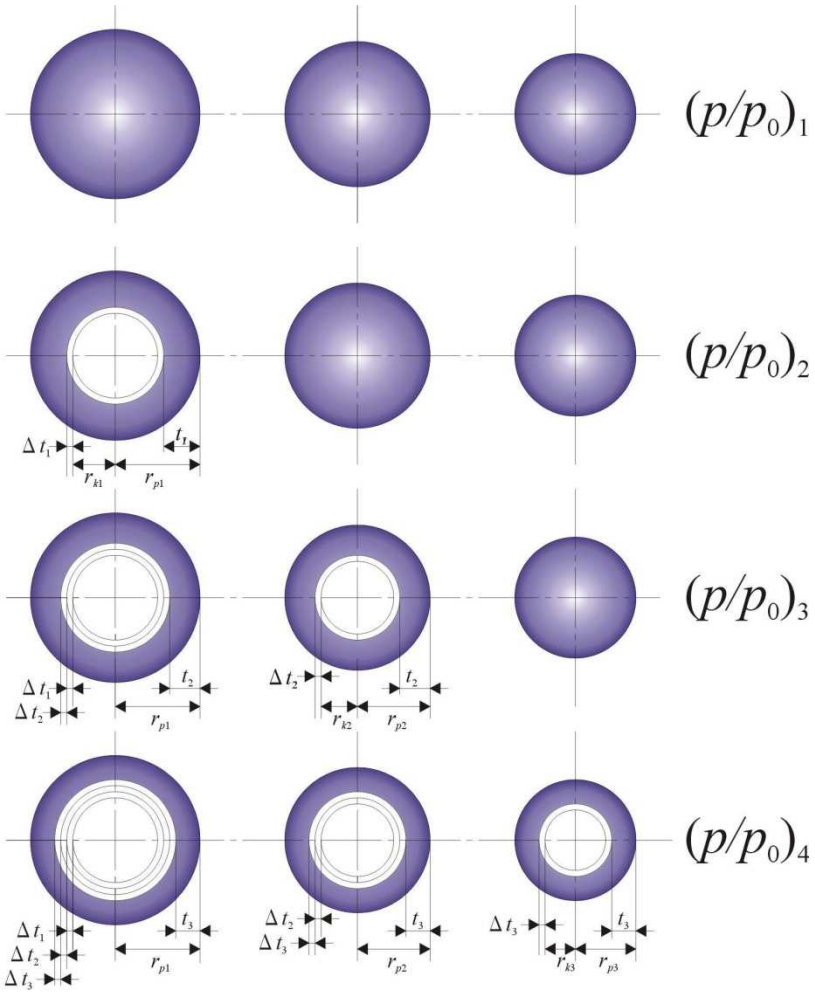
Thickness of adsorption layer can be calculated from *t* curve of standard sample, and core radius can be calculated by Kelvin equation (18.2).

$$\ln\frac{p}{p_0} = -\frac{2\gamma V_L}{RT}\frac{1}{r_m} \tag{18.2}$$

Here, r_m is meniscus radius, γ is surface tension, V_L is molar volume of liquid adsorptive, R is gas constant and T is absolute temperature. In mesopore with cyrinder shape, suppose menisucus radius at desorption is equal to core radius (r_k), and if γ and V_L of nitrogen at liquid nitrogen temperature (77 K) are applied, the following equation can be obtained.

$$r_m = 0.953/\ln(p_0/p) \tag{18.3}$$

In very fine pores, having widths of the order of a few molecular diameters, the Kelvin equation could no longer remain strictry valid. Analytical methods based on the equation give a substantial margin of error when it is applied to calculation for pores below 1–1.5 nm.



Consider a system of open ended cylindrical pores.

Assume that the relative pressure $(p/p_0)_1$, slightly lower than saturation vapor pressure and at the pressure all pores are filled with liquid.

As the pressure decreases, desorption occures. When the pressure is reduced from $(p/p_0)_1$ to $(p/p_0)_2$, a certain amount of gas, ΔV_1 is desorbed. The reduction in relative pressure result not only in emptying the largest pore of its capillary condensate, but also in a reduction in thickness of the physically adsorbed layer by the amout t_1. ΔV_1 and V_{p1}, the volume of pores which has the largest pore radius r_{p1} are expressed as follows:

$$\Delta V_1 = \pi (r_{k1} + \Delta t_1)^2 L_1 \tag{18.4}$$

$$V_{p1} = \pi r_{p1}^2 L_1 \tag{18.5}$$

where L_1 is the total length of first pore (pore radius : r_{p1}). Thus V_{p1} can be expressed as follows:

$$V_{p1} = R_1 \Delta V_1 \tag{18.6}$$

where $R_1 = r_{p1}^2 / (r_{k1} + \Delta t_1)^2$. When the pressure $(p/p_0)_2$ is lowered to $(p/p_0)_3$, ΔV_2 of gas is desorbed. ΔV_2 is not only that which comes from the second pore (pore radius: r_{p2}) but also includes that from a second thinning of the physically adsorbed layer left behind in the first layer. If the volume which is released by this thinning is designated as $V_{\Delta t2}$ then:

$$V_{p2} = R_2 (\Delta V_2 - V_{\Delta t2}) \tag{18.7}$$

where $R_2 = r_{p2}^2 / (r_{k2} + \Delta t_2)^2$. Inspection of the figure above shows that

$$V_{\Delta t2} = \pi L_1 (r_{k1} + \Delta t_1 + \Delta t_2)^2 - \pi L_1 (r_{k1} + \Delta t_1)^2 \tag{18.8}$$

Equation (18.8) is simple but in case that a greater number of pores are involved, such a calculation would become impractical. An alternative expression for $V_{\Delta t2}$ is:

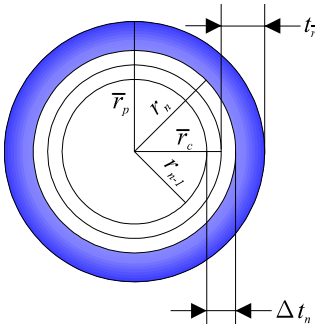
$$V_{\Delta t2} = \Delta t_2 \times Ac_1 \tag{18.9}$$

where Ac_1 is average area from which the physically adsorbed gas is desorbed. Equation (18.9) can be generalized to express $V_{\Delta tn}$ when the pressure is lowered to $(p/p_0)_n$ as follows:

$$V_{\Delta tn} = \Delta t_n \sum_{j=1}^{n-1} A_{c\,j} \tag{18.10}$$

Generalizing equation (18.7) and substituting (18.10) for $V_{\Delta tn}$ yields:

$$V_{Pn} = R_n \Delta V_n - R_n \Delta t_n \sum_{j=1}^{n-1} A_{c\,j} \tag{18.11}$$



(18.11) is complicated to carry out pore size distribution because *Ac* varies stepwise with each successive decrease in p/p_0. On the other hand A_p, the area of each pore, is a constant which can be calculated from its volume by the relationship $A_p=2V_p/r_p$. It is obvious that using A_p for calculation is more practical. Figure left represents Δt_n, change in thickness of the physically adsorpbed layer of a previously emptied pore of radius $\bar{r}_p$ during the *n*th desorption step. In a desorption step, capiraly radius changes from r_{n-1} to r_n. The average value of r_{n-1} and r_n is $\bar{r}_c$. Although *Ac* in equation (18.11) varies actually before and after a desorption step, it can be represented using $\bar{r}_c$ as follows:

$$A_c = A_p \times (\bar{r}_c / \bar{r}_p) \tag{18.12}$$

Also $\bar{r}_c$ can be described as follows:

$$\bar{r}_c = \bar{r}_p - t_{\bar{r}} \tag{18.13}$$

where $t_{\bar{r}}$ is the thickness of physically adsorbed layer at the corresponding value of (p/p_0). Equation (18.11) can be rewritten as:

$$V_{pn} = R_n \Delta V_n - R_n \Delta t_n \sum_{j=1}^{n-1} c_j A_{pj} \tag{18.14}$$

where

$$c = (\bar{r}_p - t_{\bar{r}}) / \bar{r}_p \tag{18.15}$$

$$R_n = r_{pn}^2 / (r_{kn-1} + \Delta t_n)^2 \tag{18.16}$$

c is a ratio of lateral area of two cylinders, one of which has a radius of $\bar{r}_c$ and another has a radius of $\bar{r}_p$. Even in the same pore, c value varies according to thickness of the physically adsorbed layer, i.e. c depends on the pressure. But in the original paper, they insisted that there was no big deal of error if c was treated as a constant. Then they derived equation (18.17) from equation (18.14).

$$V_{pn} = R_n \Delta V_n - R_n \Delta t_n c \sum_{j=1}^{n-1} A_{pj} \tag{18.17}$$

They recommended using 0.75, 0.8, 0.85, 0.9 as c value to make calculation simple in their original paper. And they also recommended that c value should be selected according to a peak position of pore size distribution curve. Nowadays computers have developed and we can use equation (18.14) for pore size calculation without determining c value, which makes the calculation more accurate. Pore radius can be obtained from equation (18.1), pore volume can be calculated from equation (18.14) or (18.17). Pore size distribution curve can be yieleded by plotting $\Delta V/\Delta r$ against pore radius. By summing pore volume variation

and plotting them against pore radius, cumulative pore volume curve can be obtained.

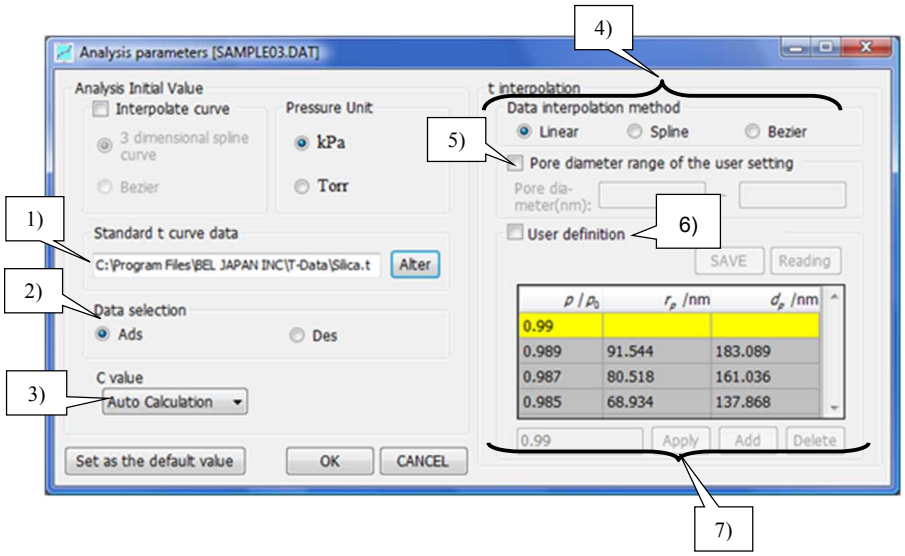
«Reference»

- "The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms", Elliott P. Barrett, Leslie G. Joyner and Paul P. Halenda, *J. Amer. Chem. Soc.*, 73, 373 (1951).

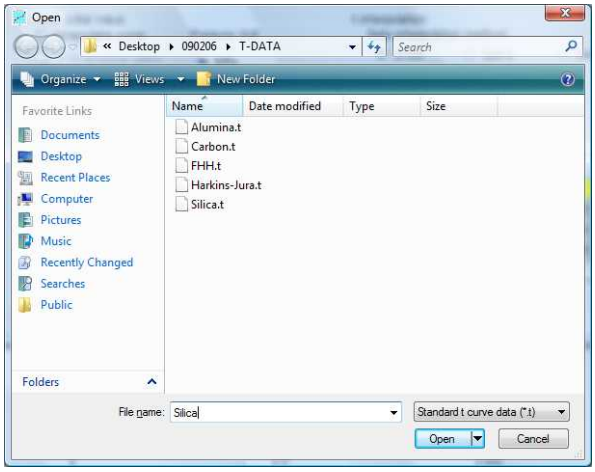
18-2. Operation

1. Select “BJH plot” on the “Analysis (A)” menu and the screen will show the following BJH plot window. The program will execute a BJH plot from adsorption or desorption data of a nitrogen adsorption isotherm.

2. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown below will appear. Change the settings as needed. For details about items not described here, see section 7-1. “Analysis parameters,” on page 37.



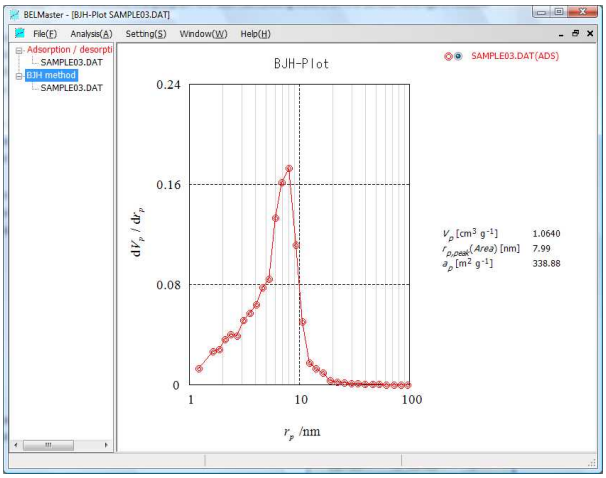
1) Select a standard t-curve.
   - Select a standard isotherm that has similar chemical characteristics to the sample surface.
   - Click on the [Alter] button and the following selection window will appear. Select a standard t-curve data file and click on the [Open] button.



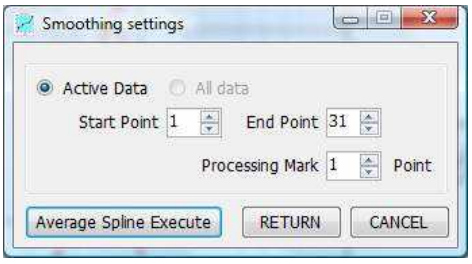
2) Select which data will be used for calculation, the adsorption branch or desorption branch.
   - Most porous samples have a pore size distribution. It is believed that distribution of pore size in these samples can be obtained from the adsorption process, and the distribution of the bottle neck can be obtained from the desorption process.
3) Select a calculation method for the C value.
   - Normally, select “Auto Calculation”. Any fixed value can be selected from 0.7, 0.75, 0.8, 0.85, or 0.9.

4) Select a method for interpolating the file data.
   - You can select Linear, Spline or Bezier.
   - If you want to execute an interpolation with the same interpolation method in an adsorption/desorption isotherm, you can check whether the interpolation method is appropriate.
5) If “Pore diameter range of the user setting” is not selected, the program will calculate using the default range. When “Pore diameter range of the user setting” is selected, the program will calculate the pore diameter range specified in the table below.
6) If “User definition” is not selected, the program will calculate the plots with the relative pressure data below. When “User definition” is selected, the program will start calculating based on the default settings of relative pressure.
7) Relative pressure settings
   - When the “User definition” is selected, this table can be edited.
   - Click on the [Apply] button and the selected cell (yellow) data will be overwritten by the value displayed in the box.
   - Click on the [Add] button and the data displayed in the box will be added.
   - The modified and added data are automatically sorted in order from top to bottom.
   - Click on the [Delete] button and the selected data will be deleted.

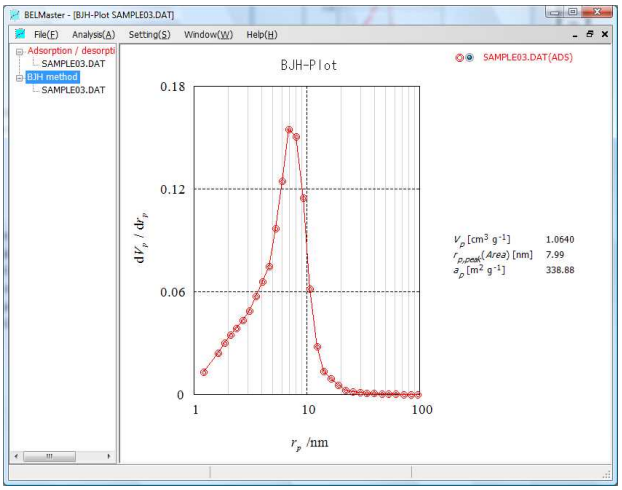
3. The figure on the right is a BJH-plot (differential curve) of a nitrogen adsorption isotherm for mesoporous silica. “silica-BEL.t” is used as a standard isotherm.



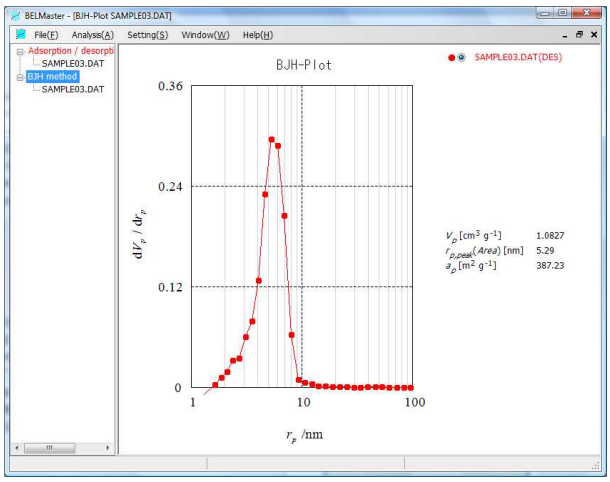
4. When you want to smooth the data, select “Smoothing settings” on the “Setting” menu. The “Smoothing settings” window shown on the right will appear.



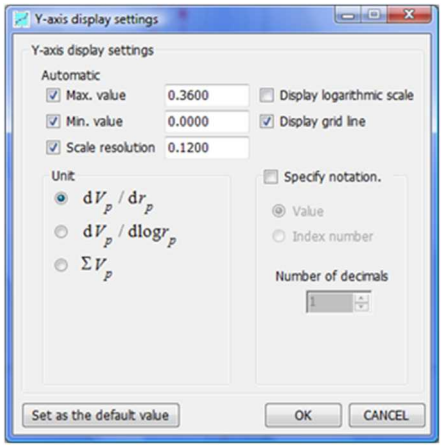
5. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 2 to 15 nm radius, and it has a distribution peak at 8.0 nm. The integrated pore volume (V_p) will be 1.064 cm^3 g^{-1}.



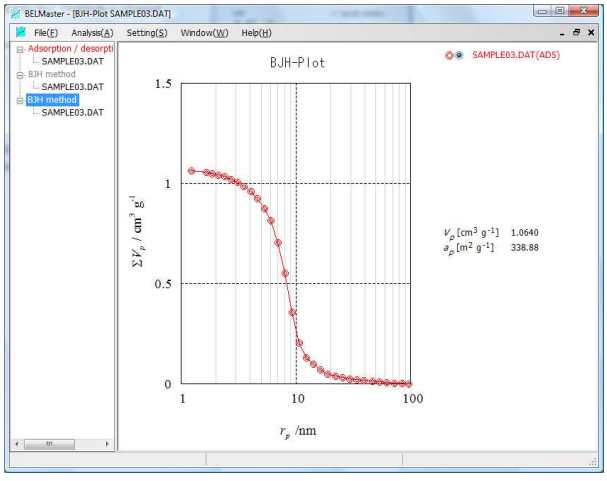
6. For this silica, select the desorption process on the "Analysis parameters" window. The figure on the right shows a result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 3 to 9 nm radius at its neck, and has a distribution peak at 5.3 nm.



7. In a BJH plot, the Y axis units can be set to "dV_p/dr_p," "$dV_p/d\log r_p$," or "ΣV_p" in "Y axis display settings" on the "Settings (S)" menu. Integrated graphs (integral curve) are shown from a larger pore size.
   - "dV_p/dr_p" ---is the area distribution.
   - "$dV_p/d\log r_p$" --- is the volume distribution. Distribution of larger diameter are bolded.
   - "ΣV_p" --- is an integral curve.



8. The figure on the right is a BJH plot (integral curve) of the silica described before calculated from adsorption branch of its isotherm.



Chapter 19: CI plot

19-1. Description

CI method is the way to calculate pore size distribution using Kelvin equation like BJH method. Cranston and Inkley proposed this method in 1957. They insisted that their method was superior to BJH method in some aspects below:

1) CI method is more exact than BJH method.
2) CI method can be applied either adsorption or desorption branch.
3) Comparing surface area from CI method and from BET method provides a measure of the validity of physical assumptions.

It is assumed that pores are cylindrical in shape with one end closed. Although the adsorption branch is adopted for derivation as follows, it does not mean that this method cannot be applied to the desorption branch. At a relative pressure p_r, all pores which radius is smaller than r are filled with adsorbate and pores with radii larger than r contain adsorbed layer and of thickness t_r. Let $V_r\delta r$ be the volume of pores having radii between r and $r\square\delta r$, where δr is very small campared with r.

Consider an adsorption step from a relative pressure p_r to $p_{r+\delta r}$. Due to this pressure increase, capillary condensation occurs in the pores with radii from r to $r+\delta r$. At the same time the thickness of adsorbed layer increases from t_r to $t_r+\delta t$ in the pores with radii larger than $r+\delta r$.

As a result adsorbed amount increases by $v_r\delta r$:

$$v_r\delta r = \frac{(r-t_r)^2}{r^2}V_r\delta r + \delta t\int_{r+\delta r}^{\infty}\frac{r-t_r}{r}\frac{2V_r}{r}dr \tag{19.1}$$

The first term of the right-hand side represents the volume of nitrogen which has gone to fill pores, while the second term represents the volume of nitrogen which has contributed to increasing the thickness of the adsorbed layer. In the limiting case, where δr tends to zero, equation (19.1) can be rewritten as follows.

$$v_r dr = \frac{(r-t_r)^2}{r^2}V_r dr + dt\int_{r}^{\infty}\frac{2V_r(r-t_r)}{r^2}dr \tag{19.2}$$

Consider a finite adsorption step from p_1 to p_2. With the change in pressure, critical radius varies from r_1 to r_2 and the adsorbed layer thickness varies from t_1 to t_2. v_{12}, the increased amount adsorbed in this adsorption step, can be expressed as follows:

$$v_{12} = \int_{r_1}^{r_2}v_r dr = \int_{r_1}^{r_2}\frac{(r-t_1)^2}{r^2}V_r dr + (t_2-t_1)\int_{r_2}^{\infty}\frac{V_r(2r-t_1-t_2)}{r^2}dr \tag{19.3}$$

Assuming V_r is sensibly constant over the range r_1 to r_2. This assumption is valid when the difference between r_1 and r_2 is enough small. (19.3) can be converted into (19.4).

$$v_{12} = \frac{V_{12}}{r_2-r_1}\int_{r_1}^{r_2}\frac{(r-t_1)^2}{r^2}dr + (t_2-t_1)\int_{r_2}^{\infty}\frac{V_r(2r-t_1-t_2)}{r^2}dr \tag{19.4}$$

where V_{12} is the volume of pores with radii between r_1 and r_2. To calculate pore volume, (19.4) is transformed as follows:

$$V_{12} = R_{12}\left(v_{12} - k_{12}\int_{r_2}^{\infty}\frac{r-t_{12}}{2r^2}V_r dr\right) \tag{19.5}$$

where

$$R_{12} = \frac{r_2 - r_1}{\int_{r_1}^{r_2} \left[(r - t_1)^2 / r^2 \right] dr} \tag{19.6}$$

$$k_{12} = 4(t_2 - t_1) \tag{19.7}$$

$$t_{12} = \frac{t_1 + t_2}{2} \tag{19.8}$$

The integral term in equation (19.5) is replaced by a summation term.

$$V_{12} = R_{12} \left(v_{12} - k_{12} \sum_{r_2 + \frac{1}{2}\Delta r}^{r\,\max} \frac{r - t_{12}}{2r^2} V_r \Delta r \right) \tag{19.9}$$

Equation (19.10) can be derived by replacing pore radius in equation (19.9) to pore diameter.

$$V_{12} = R_{12} \left(v_{12} - k_{12} \sum_{d_2 + \frac{1}{2}\Delta d}^{d\,\max} \frac{d - 2t_{12}}{d^2} V_r \Delta d \right) \tag{19.10}$$

Cranston *et al.* made a table for R_{12} and k_{12} from isotherms on 15 nonporous materials prior to pore size distribution. Also they made a table for $(d - 2t_{12}) / d^2$ to simplify the calculation. Recently computer has developed. Calculating $(d - 2t_{12}) / d^2$ value against each pore size is not so hard and the calculation result is more accurate. In our software, calcuration is carried out as such.

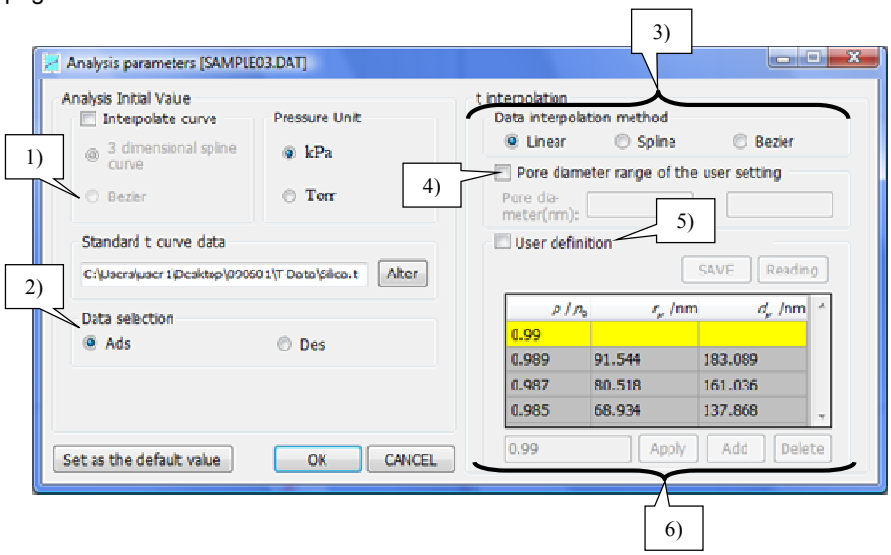
«Reference»

- "The Determination of Pore Structures from Nitrogen Adsorption Isotherms", R. W. Cranston and F. A. Inkley, *Advan. Catalysis,* 9, 143 (1957).

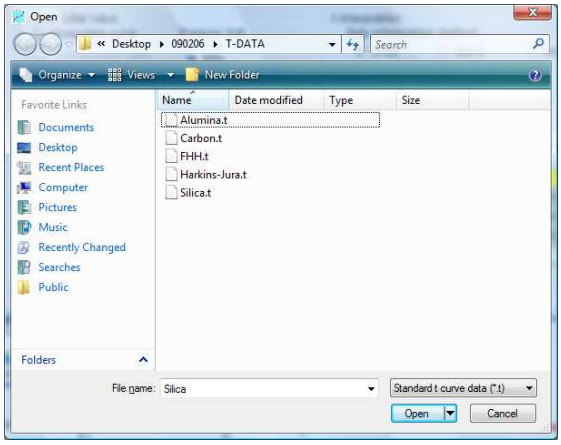
19-2. Operation

1. Select “CI plot” on the “Analysis (A)” menu and the screen will show the following CI plot windows.
   The program will execute a CI plot from adsorption or desorption data of a nitrogen adsorption isotherm.

2. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown below will appear. Change the settings as needed. For details about items not described here, see section 7-1. “Analysis parameters,” on page 37.



1) Select a standard t-curve.
   - Select a standard isotherm that has similar chemical characteristics to the sample surface.
   - Click on the [Alter] button and the following selection window will appear. Select a standard t-curve data file and click on the [Open] button.



2) Select which data will be used for calculations, the adsorption side or desorption side.
   - Most mesopore samples have a distribution of pore sizes. In these samples, it is assumed that pore size distribution can be obtained from the adsorption process, and the distribution of the bottle neck can be obtained from the desorption process.
3) Select a method for interpolating the file data.
   - You can select Linear, Spline or Bezier.
   - In an adsorption/disorption isotherm, if you want to execute an interpolation using the same interpolation method, you can check whether the interpolation method is appropriate.
4) If “Pore diameter range of the user setting” is not selected, the program will calculate using the default range. When “Pore diameter range of the user setting” is selected, the program will calculate the pore diameter range

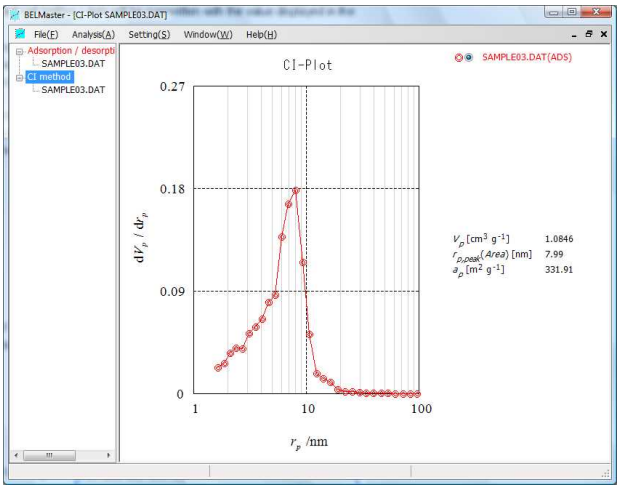
specified in the table below.

5) If “User definition” is not selected, the program will calculate the plots with the relative pressure data below. When “User definition” is selected, the program will start calculating based on the default settings of relative pressure.

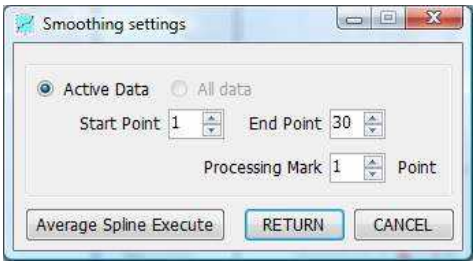
6) Relative pressure settings.

- When the “User definition” is selected, this table can be edited.
- Click on the [Apply] button and the selected cell (yellow) data will be overwritten by the value displayed in the box.
- Click on the [Add] button and the data displayed in the box will be added.
- The modified and added data are automatically sorted in order from top to bottom.
- Click on the [Delete] button and the selected data will be deleted.

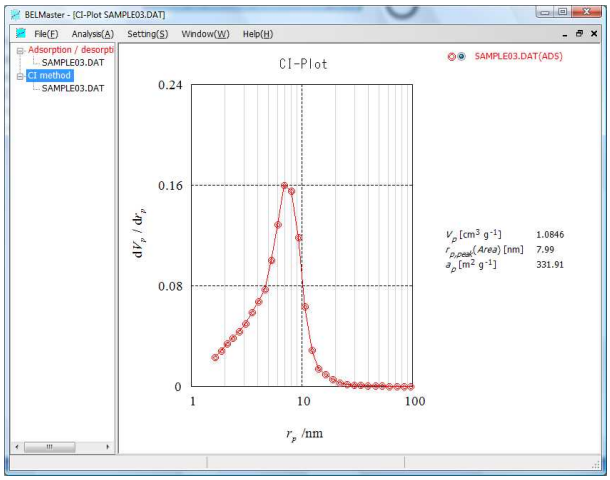
3. The figure on the right is a CI-plot (differential curve) of a nitrogen adsorption isotherm for mesoporous silica. “silica-BEL.t” is used as a standard isotherm.



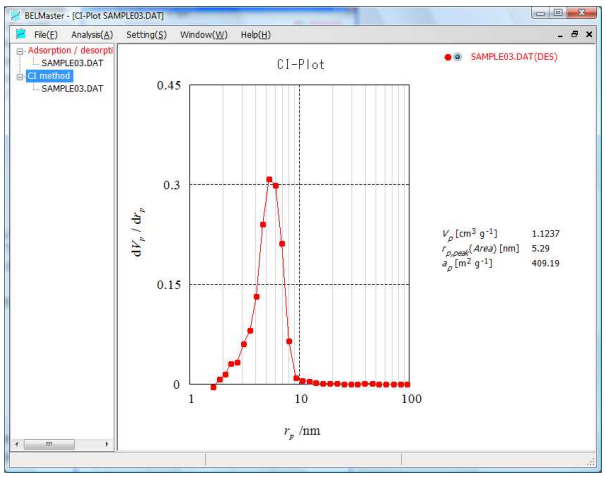
4. When you want to smooth the data, select “Smoothing settings” on the “Settings” menu. The “Smoothing settings” window shown on the right will appear.



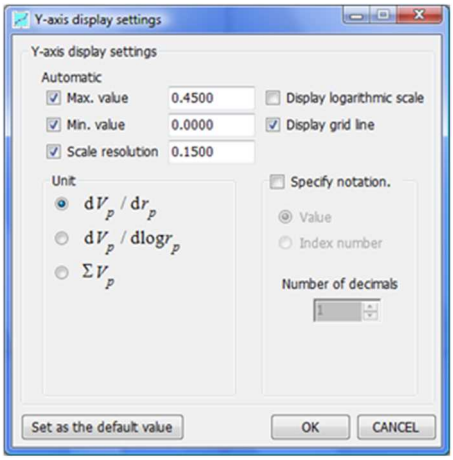
5. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 2 to 15 nm radius, and has a distribution peak at 8.0 nm. The integrated pore volume (V_p) will be 1.085 cm^3 g^{-1} and the integrated pore area (a_p) is 332 m^2 g^{-1}.



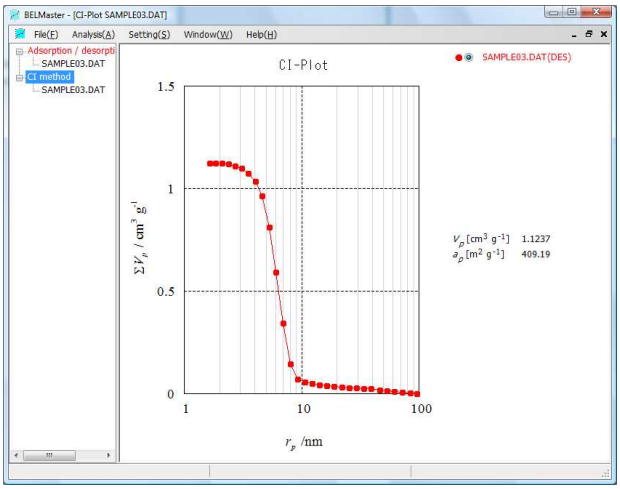
6. Select the desorption process to use for this silica sample on the “CI-plot setting” window. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 3 to 9 nm radius, and has a distribution peak at 5.3 nm.



7. In a CI plot, the Y axis units can be set to “dV_p/dr_p,” “$dV_p/d\log r_p$”, or “ΣV_p” in “Y axis display settings” on the “Setting(S)” menu. Integrated graphs (integral curve) are shown from a larger pore size.
   - “dV_p/dr_p” ---is the area distribution.
   - “$dV_p/d\log r_p$” --- is the volume distribution. Distribution of larger diameter are bolded.
   - “ΣV_p” --- is an integral curve.



8. The figure on the right is a CI plot (integral curve) of the silica described before calculated from adsorption branch of its isotherm.



Chapter 20: DH plot

20-1. Description

DH-method is based on Kelvin equation and used to calculate pore size distribution like BJH and CI method. Dollimore and Heal proposed this method in 1964. Complex assumptions are not required and calculations are simple.

Assume that pores are cyrindrical in shape with one ends closed. As the pressure is lowered stepwise from saturation pressure, desorption occurs. Let the critical radius when the *n*th step of desorption occurs, r_{p_n}. Total volume of pores which are still filled with adsorbate after the *n*th step of desorption, $V[>r_{p_n}]$, can be described as follows:

$$V[<r_{p_n}] = \int_0^{r_{p_n}} \pi r_p^{\,2} L(r_p) dr_p \tag{20.1}$$

Also the length and the surface area of pores which are emptied before the *n*th step of desorption, $A[>r_{p_n}]$ and $L[>r_{p_n}]$ can be expressed as follows:

$$A[>r_{p_n}] = \int_{r_{p_n}}^{\infty} 2\pi r_p L(r_p) dr_p \tag{20.2}$$

$$L[>r_{p_n}] = \int_{r_{p_n}}^{\infty} L(r_p) dr_p \tag{20.3}$$

where $L(r_p)$ expresses the length of pores which has radius of r_p. It is a continuous function of r_p.

ΔV_n, the amount desorbed by the *n*th step of desorption is:

$$\Delta V_c = \Delta V_n - \Delta V_m \tag{20.4}$$

where ΔV_c is the sum of capillary desorption and ΔV_m is the total of multilayer desorption. At this time, the volume of adsorbate in a pore of radius $r_p (> r_{p_n})$ can be represented as follows:

$$\pi[r_p^{\,2} - (r_p - t_n)^2] L(r_p) = \pi(2r_p t_n - t_n^{\,2}) L(r_p) \tag{20.5}$$

where t_n is the thickness of multilayer for the step n. The total multilayer adsorption in all pores or radii from r_{p_n} to ∞ can be calculated by integration of (20.5) and the result can be rewritten by using (20.2) and (20.3) as follows.

$$\begin{aligned} V_m &= \int_{r_{p_n}}^{\infty} \pi(2r_{p_n} - t_n^{\,2}) L(r_p) dr_p \\ &= t_n \int_{r_{p_n}}^{\infty} 2\pi r_p L(r_p) dr_p - \pi t_n^{\,2} \int_{r_{p_n}}^{\infty} L(r_{p_n}) dr_p \\ &= t_n A[>r_{p_n}] - \pi t_n^{\,2} L[>r_{p_n}] \end{aligned} \tag{20.6}$$

By differentiating (20.6) with respect to t_n, equation (20.7) can be obtained and the volume change on nth desorption step, ΔV_m, can be calculated from the eauation.

$$dV_m = dt_n A[>r_{p_n}] - \pi 2 t_n dt_n L[>r_{p_n}] \tag{20.7}$$

Changing to Δ terms for finite steps:

$$\Delta V_m = \Delta t_n A[>r_{p_n}] - \pi 2 t_n \Delta t_n L[>r_{p_n}] \tag{20.8}$$

$A[>r_{p_n}]$, $L[>r_{p_n}]$ may be put in finite terms also, as the summations of length and area of pores involved in previous steps:

$$\Delta V_m = \Delta t_n \sum A_p - \pi 2 t_n \Delta t_n \sum L_p \tag{20.9}$$

From equation (19.4) and (19.8), equation (19.10) can be obtained.

$$\Delta V_c = \Delta V_n - \Delta t_n \sum A_p + \pi 2 t_n \Delta t_n \sum L_p \tag{20.10}$$

By using equation (19.10), the change of pore volume ΔV_p can be calculated from ΔV_c.

$$\begin{aligned} \Delta V_p &= [r_p /(r_k + \Delta t)]^2 \Delta V_c \\ &= R_n \Delta V_c \end{aligned} \tag{20.11}$$

where

$$R_n = [r_p /(r_k + \Delta t)]^2 \tag{20.12}$$

Thus equation (19.10) can be rewritten as follows:

$$\Delta V_p = R_n (\Delta V_n - \Delta t_n \sum A_p + \pi 2 t_n \Delta t_n \sum L_p) \tag{20.13}$$

The increasing surface area of pores when desorption occures, A_p can be obtained by next equation.

$$A_p = 2\Delta V_p / r_p \tag{20.14}$$

And L_p, the length of the pores can be represented as follows:

$$L_p = A_p / 2\pi r_p \tag{20.15}$$

These two terms are summed line by line pore size distribution can be obtained by using equation (20.13).

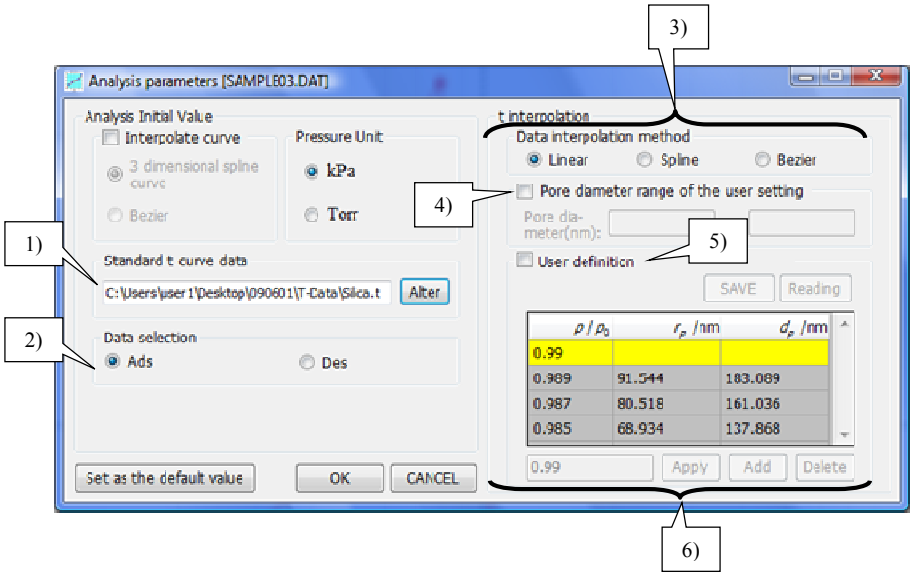
«Reference»

- D. Dollimore and G. R. Heal, *J. Applied Chem.* 14, 109 (1964); *J. Colloid Interfasce Sci.* 33, 508 (1970).

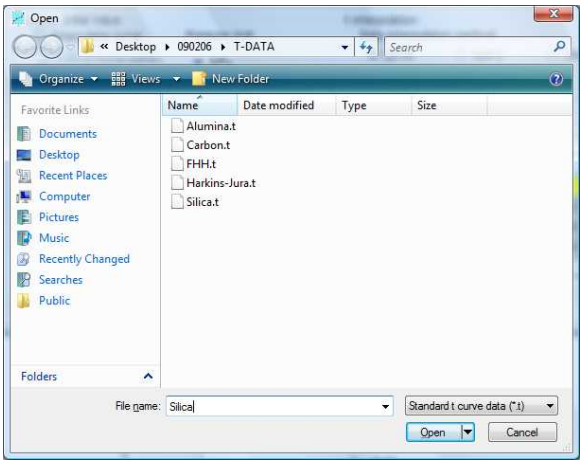
20-2. Operation

1. Select “DH plot” on the “Analysis (A)” menu and the screen will show the following DH plot windows. The program will execute a DH plot from adsorption or desorption data of a nitrogen adsorption isotherm.

2. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown below will appear. Change the settings as needed. For details about items not described here, see section 7-1. “Analysis parameters,” on page 37.



1) Select a standard t-curve.
   - Select a standard isotherm that has similar chemical characteristics as the sample surface.
   - Click on the [Alter] button and the following selection window will appear. Select a standard t-curve data file and click on the [Open] button.



2) Select which data will be used for calculations, the adsorption side or desorption side.
   - Most mesopore samples have a distribution of pore sizes. In these samples, it is assumed that pore size distribution can be obtained from the adsorption process, and the distribution of the bottle neck can be obtained from the desorption process.

3) Select a method for interpolating the file data.
   - You can select Linear, Spline or Bezier.
   - In an adsorption/disorption isotherm, if you want to execute an interpolation using the same interpolation

method, you can check whether the interpolation method is appropriate.

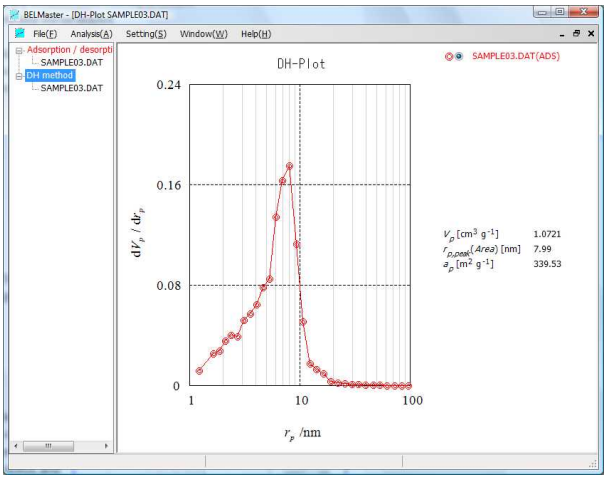
4) If “Pore diameter range of the user setting” is not selected, the program will calculate using the default range. When “Pore diameter range of the user setting” is selected, the program will calculate the pore diameter range specified in the table below.

5) If “User definition” is not selected, the program will calculate the plots with the relative pressure data below. When “User definition” is selected, the program will start calculating based on the default settings of relative pressure.

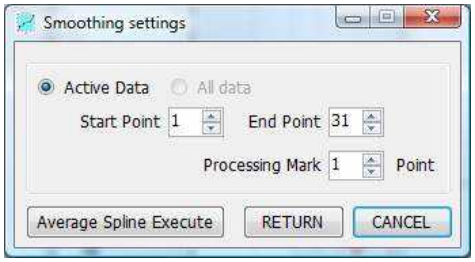
6) Relative pressure settings.

- When the “User definition” is selected, this table can be edited.
- Click on the [Apply] button and the selected cell (yellow) data will be overwritten by the value displayed in the box.
- Click on the [Add] button and the data displayed in the box will be added.
- The modified and added data are automatically sorted in order from top to bottom.
- Click on the [Delete] button and the selected data will be deleted.

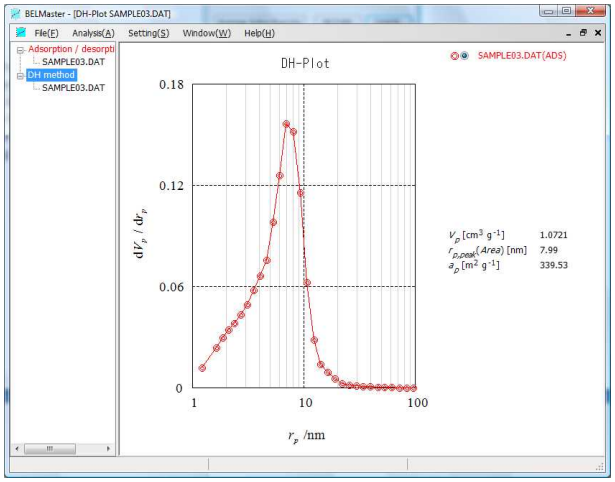
3. The figure on the right is a DH-plot (differential curve) of a nitrogen adsorption measurement on mesoporous silica. “silica-BEL.t” is used as a standard isotherm.



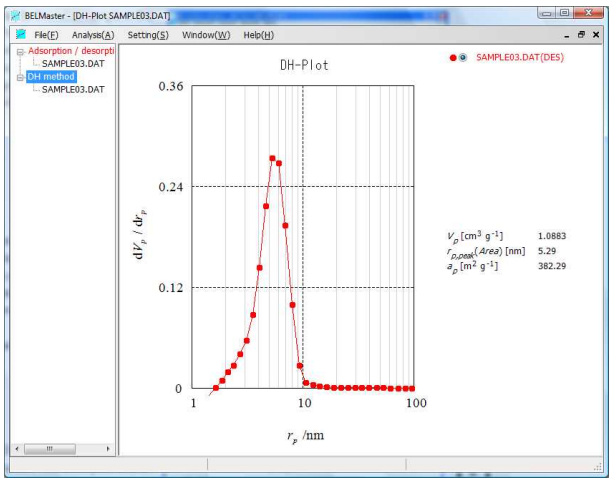
4. When you want to smooth the data, select “Smoothing settings” on the “Settings” menu. The “Smoothing settings” window shown on the right will appear.



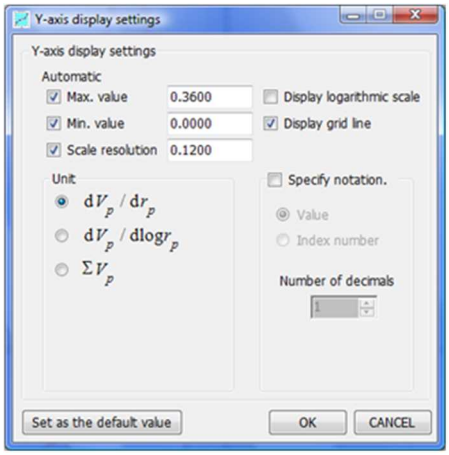
5. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 2 to 15 nm radius, and has a distribution peak at 8.0 nm. The integrated pore volume (V_p) will be 1.07 cm^3 g^{-1} and the integrated pore area (A_p) is 340 m^2 g^{-1}.



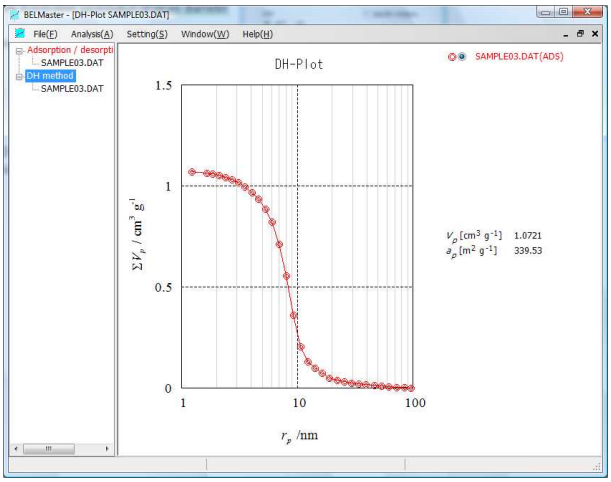
6. Select the desorption process for this silica sample in the “DH-plot setting” window. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 3 to 9 nm radius, and has a distribution peak at 5.3 nm.



7. The Y axis units in a DH plot can be set to “dV_p/dr_p”, “$dV_p/d\log r_p$” or “ΣV_p ” on “Y axis display settings” in the “Setting (S)” menu. The integrated graphs (integral curve) are shown from a larger pore size.
   - “dV_p/dr_p” ---is the area distribution.
   - “$dV_p/d\log r_p$” --- is the volume distribution.
     Distribution of larger diameter are bolded.
   - “ΣV_p” --- is an integral curve.



8. The figure on the right is a DH plot (integral curve) of the silica described before calculated from adsorption branch of its isotherm.

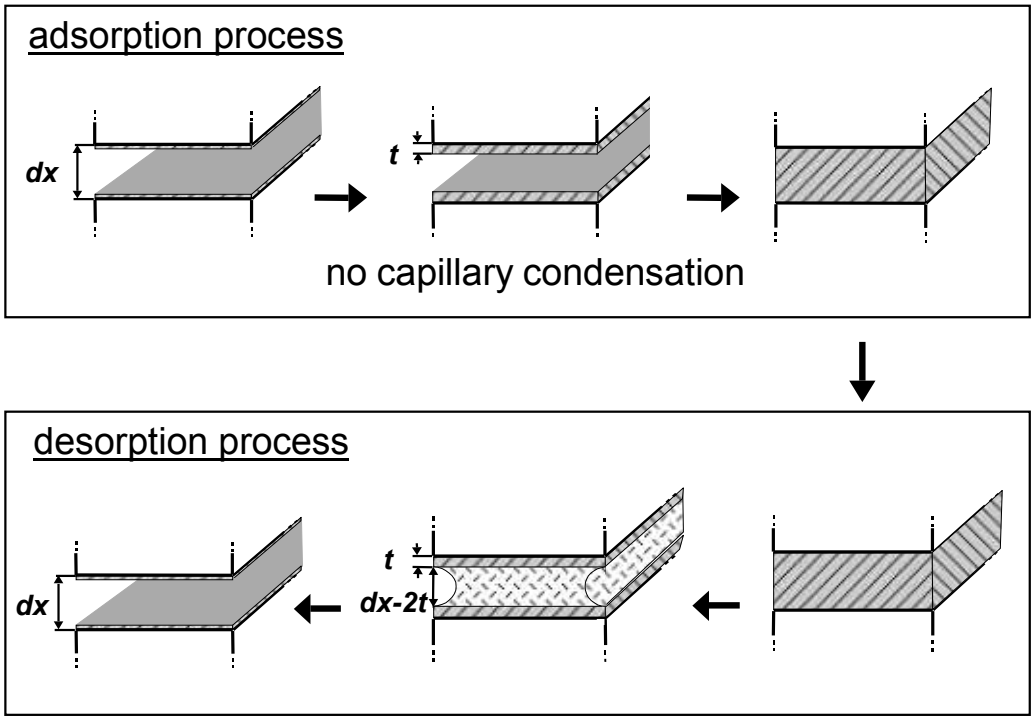


Chapter 21: INNES plot

21-1. Description

To calculate pore distribution for mesopores (pore width: 2 to 50 nm) by using nitrogen adsorption isotherms, you must select the pore shape. At first, generally classify the shape of mesopores into slit shape and other shapes (such as cylindrical, ink bottle-shaped).

For analysis of slit-shaped mesopores, capillary condensation will not occur in adsorption branches of adsorption isotherms. When t-plotting is executed for an adsorption branch, a straight line passing through the origin is obtained in a range of t = 0 to 1.0 nm.



On the other hand, for analysis of mesopores of other than slit shape (cylindrical mesopores, ink-bottle mesopores, etc.), capillary condensation occurs in adsorption branches of adsorption isotherms.

When t-plotting is executed for an adsorption branch, a straight line passing through the origin is obtained in a range of t = 0 to 0.5 nm. However, upper deviation attributable to capillary condensation is observed in a range of t = 0.5 nm or more. Therefore, t-plotting is effective in differentiation of mesopore shapes.

When the width of slit-shaped mesopores is indicated as "*dx*", and the thickness of adsorption layer is indicated as "*t*", the meniscus generated in slit-shaped mesopores is hemicylindrical shape. Kelvin equation for hemicylindrical meniscus is given as (1):

$$ln\left(\frac{p}{p_0}\right) = -\frac{2\gamma V_L}{RT}\frac{1}{(dx - 2t)} \qquad (21\text{-}1)$$

Now, we will compare the Kelvin equation for slit-shaped mesopores with that for cylindrical mesopores. Shape of meniscus generated in cylindrical mesopores is hemispherical. Kelvin equation for hemispherical meniscus is given as (2):

$$ln\left(\frac{p}{p_0}\right) = -\frac{2\gamma V_L}{RT}\frac{1}{r_K} \qquad (21\text{-}2)$$

In comparison between equations (21-1) and (21-2), we can see that r_K (Kelvin radius) for cylindrical mesopores corresponds to $(dx - 2t)$ in the equation for slit-shaped mesopores.

Before calculation of mesopore distribution, substitute the following values into equation (21-1).

Substitute γ = 8.85 x 10^{-3} N m^{-1}, V_L = 34.71 cm^3 mol^{-1}, T = 77.35 K and R = 8.3145 J mol^{-1} K^{-1} into equation (21-1). Then, equation (21-3) is obtained.

$$(dx - 2t) = -\frac{0.415}{\log_{10}(p/p_0)} \text{ nm} \qquad (21\text{-}3)$$

Regarding the slit-shaped mesopore as a parallel plate mode, the following equation is established.

$$X = V + At \qquad (21\text{-}4)$$

X = Amount (cm^3g^{-1}) of nitrogen (adsorptive) adsorbed in liquid state
V =Volume (cm^3g^{-1}) of nitrogen in liquid state when slit-shaped mesopore is fully filled
A = Surface area (m^2g^{-1}) of slip-shaped mesopore when the pore is not fully filled

In consideration of the change in amount of adsorption (X) and mesopore volume (V), the amount of change can be expressed with the following equation, by using an average value (A_{ave}) of surface area (A) and an average value (t_{ave}) of adsorptive thickness (t).

$$\Delta X_{(i)} = \Delta V_{(i)} + A_{(i)ave}\Delta t_{(i)} + t_{(i)ave}\Delta A_{(i)} \qquad (21\text{-}5)$$

ΔV can be expressed with the following equation, by using an average value (d_{ave}) of the slit diameter.

$$\Delta V_{(i)} = \frac{-d_{(i)ave}\Delta A_{(i)}}{2} \qquad (21\text{-}6)$$

Substitute equation (21-6) into equation (21-5). Then, the following equation is established.

$$\Delta X_{(i)} = \Delta V_{(i)} + A_{(i)ave}\Delta t_{(i)} - \frac{2t_{(i)ave}}{d_{(i)ave}}\Delta V_{(i)} \qquad (21\text{-}7)$$

Transform equation (7) to make equation (8).

$$\Delta V_{(i)} = \frac{d_{(i)ave}}{d_{(i)ave} - 2t_{(i)ave}}(\Delta X_{(i)} - A_{(i)ave}\Delta t_{(i)}) \qquad (21\text{-}8)$$

It is considered that the adsorptive is saturated in slit-shaped mesopores around high relative pressure. Therefore, equations $V_{(0)} = X_{(0)}$ and A = 0, and the equation (21-9) are established. Thus, ΔV can be obtained in each step:

$$A_{(i+1)}ave = A_{(i)} + \Delta A_{(i+1)} \qquad (21\text{-}9)$$

From the above equation, ΔA can be approximately expressed with the equation below.

$$\Delta A_{(i)} = \frac{\Delta X_{(i)}}{\Delta d_{(i)ave}} \times \frac{\Delta V_{(i-1)}}{\Delta X_{(i-1)}} \qquad (21\text{-}10)$$

Create a pore distribution curve by using “dx” obtained with equation (21-3), and “ΔV” obtained with equation (21-8).

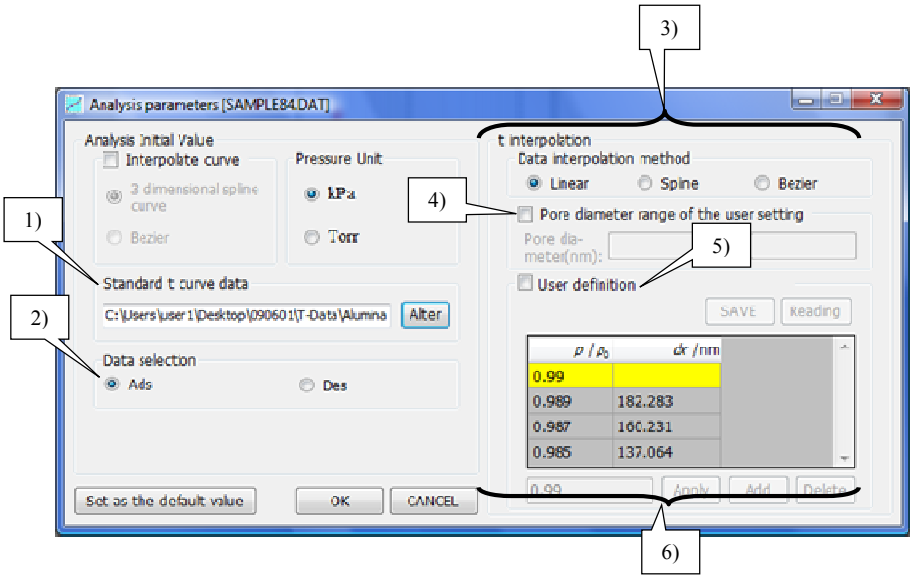
«Reference»

- F. Rouquerol, J. Rouquerol & K. Sing “Adsorption by powders & porous solids (Academic Press, 1999)”, 440
- W. B. INNES “Analytical Chemistry”, 29, 1069 (1957).

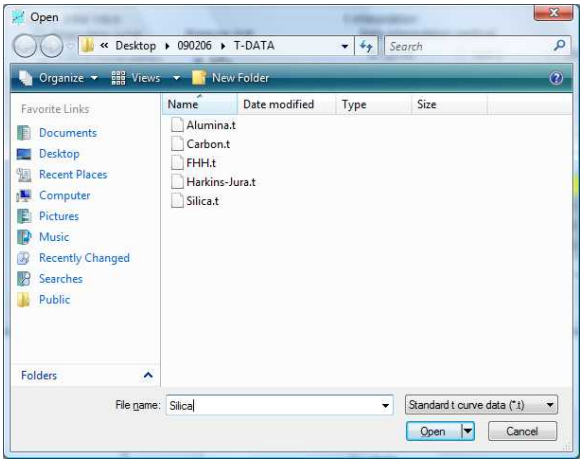
21-2. Operation

1. Select “INNES method” on the “Analysis (A)” menu and the screen will show the followimg INNES-plot windows. The program will execute a INNES plot from adsorption or desorption of a nitrogen adsorption isotherm.

2. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown below will appear. Change the settings as needed. For details about items not described here, see section 7-1 “Analysis parameters” on page 37.



1) Select a standard t-curve.
   - Select a standard isotherm that has similar chemical characteristics as the sample surface.
   - Click on the [Alter] button and the following selection window will appear. Select a standard t-curve data file and click on the [Open] button.



2) Select which data will be used for calculations, the adsorption side or desorption side.
   - To calculate pore distribution for slit-shaped mesopores, use desorption isotherm. For pore distribution calculation, do not use adsorption isotherm, because capillary condensation is not observed in adsorption isotherm.
3) Select a method for interpolating the file data.
   - You can select Linear, Spline or Bezier.
   - In an adsorption/disorption isotherm, if you want to execute an interpolation using the same interpolation

method, you can check whether the interpolation method is appropriate.

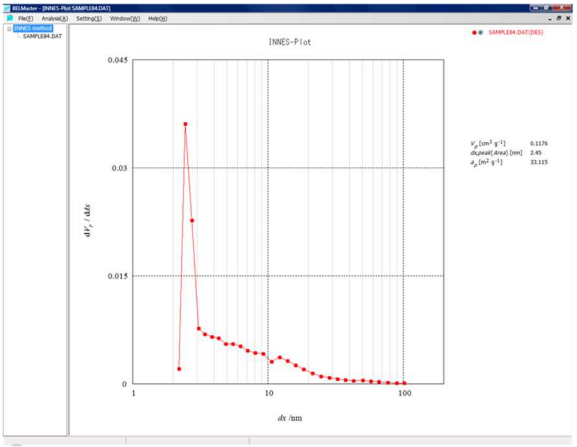
4) If “Pore diameter range of the user setting” is not selected, the program will calculate using the default range. When “Pore diameter range of the user setting” is selected, the program will calculate the pore diameter range specified in the table below.

5) If “User definition” is not selected, the program will calculate the plots with the relative pressure data below. When “User definition” is selected, the program will start calculating based on the default settings of relative pressure.

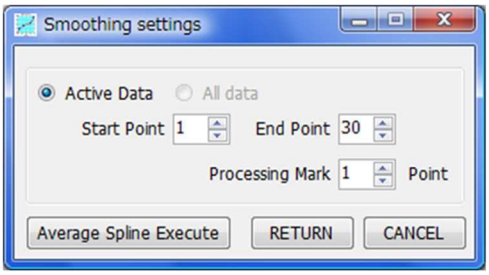
6) Relative pressure settings.

- When the “User definition” is selected, this table can be edited.
- Click on the [Apply] button and the selected cell (yellow) data will be overwritten by the value displayed in the box.
- Click on the [Add] button and the data displayed in the box will be added.
- The modified and added data are automatically sorted in order from top to bottom.
- Click on the [Delete] button and the selected data will be deleted.

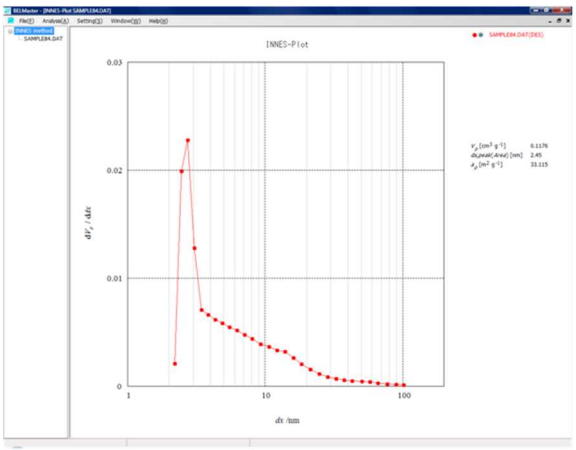
3. The figure on the right shows an INNES-plot curve (differential curve) obtained with measurement (desorption process) of nitrogen adsorption into a clay mineral with slit-shaped pores. “alumina-BEL.t” is specified as a standard isotherm.



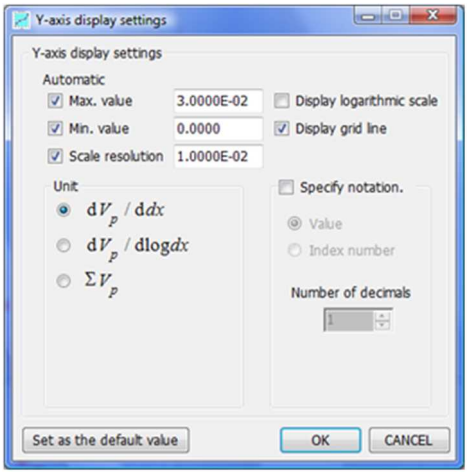
4. When you want to smooth the data, select “Smoothing settings” on the “Settings” menu. The “Smoothing settings” shown on the right will appear.



5. Select the desorption process for this clay mineral sample in the “INNES-plot setting” window. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 2 to 15 nm radius, and has a distribution peak at 2.5 nm. The integrated pore volume (V_p) is 0.118 $cm^3\ g^{-1}$, and the integrated pore area (A_p) is 33.2 $m^2\ g^{-1}$.



6. The Y axis units in an INNES plot can be set to "dV_p/dr_p", "$dV_p/d\log r_p$" or "ΣV_p " on "Y axis display settings" in the "Setting (S)" menu. The integrated graphs (integral curve) are shown from a larger pore size.
   - "dV_p/dr_p" ---is the area distribution.
   - "$dV_p/d\log r_p$" --- is the volume distribution.
     Distribution of larger diameter are bolded.
   - "ΣV_p" --- is an integral curve



Chapter 22: DA plot

22-1. Description

In 1960, Dubinin and Radushkevich introduced DA equation that they derived from adsorption potential theory of Polanyi. Polanyi hypothesized that pressure of adsorptive when it is adsorbed is equal to the saturated vapor pressure p_0 of its gas. Expressing pressure of adsorptive(adsorption molecule that is not adsorbed) as p, work of transferirng 1 mol of gas from gas phase to adsorption layer ε can be expressed as the following.

$$\varepsilon = RT\ln(p_0 / p) \tag{22.1}$$

Polanyi defined ε as adsorption potential. ε can be replaced by Gibbs free energy change $-\Delta G$ at adsorption.

$$\varepsilon = -\Delta G \tag{22.2}$$

Dubinin thought that adsorption into pores progresses by volume filling but not building up adsorption layer one by one. Then he defines the filling factor θ by the following equation.

$$\theta = V / V_p \tag{22.3}$$

V_p indicates whole micropore volume, V means pore volume at relative pressure p/p_0. θ is also the function of relative pressure thus the function of ε from (22.1).

$$\theta = f(\varepsilon / \beta) \tag{22.4}$$

β is a specific constant number for adsorbate and is called affinity coefficient. With a hypothesis that pore makes Gaussian distribution, the following equation is obtained.

$$\theta = \exp\left[-k\left(\frac{\varepsilon}{\beta}\right)^2\right] \tag{22.5}$$

k is a constant number that depends on pore structure. The following equation is obtained from (22.3), (22.4) and (22.5).

$$V = V_p \exp\left[-\frac{k}{\beta^2}\{RT\ln(p_0 / p)\}^2\right] \tag{22.6}$$

or,

$$\frac{V}{V_p} = \exp\left[-B\left(\frac{T}{\beta}\right)^2 \log_{10}^2(p_0 / p)\right] \tag{22.7}$$

where b is a constant represented by equation (22.8).

$$B = 2.303R^2 / k \tag{22.8}$$

(22.7) can be coverted to

$$\log_{10} V = \log_{10} V_p - C\log_{10}^2(p_0 / p) \tag{22.9}$$

where

$$C = B\left(\frac{T}{\beta}\right)^2 \tag{22.10}$$

(22.6), (22.7) and (22.9) are called DR equation. If you convert adsorption amount to V using adsorbate density at its liquid condition, and then plot $\log_{10} V$ against $\log_{10}^2(p_0 / p)$ (DR-plot), you wil get a linear curve with the intercept $\log_{10} V_p$ and the slope C. V_p is whole micropore volume.

In 1971, Dubinin and Astakov extended the concept of DR equation and made it more common form.

The derived equation is called DA equation expressed as follows.

$$\theta = \exp\left[-\left(\frac{RT}{\varepsilon}\right)^n \ln^n\left(p_0 / p\right)\right] \tag{22.11}$$

or,

$$\log_{10} V = \log_{10} V_p - C' \log^n_{10}(p_0 / p) \tag{22.12}$$

where C' can be given by equation (22.13).

$$C' = 2.303^{n-1}\left(\frac{RT}{\varepsilon}\right)^n \tag{22.13}$$

In the same manner as DR-plot, V_p is calculated from the linear slope value that is obtained by plotting $\log_{10} V$ against $\log^n_{10}(p_0 / p)$. n is a small integral number (normally 1~3). Kawazoe et al. categorized adsorbate molecule diameters expressing adsorbate molecule diameter as d and pore size as D like the following table. Applying m=2 to DA equation, it becomes DR equation.

Adsorption site	Ratio	n
Surface	$D/d > 5$	1
Micropore	$5 > D/d > 3$	2
Ultramicropore	$3 > D/d$	3

DA method is often used for calculation of pore volume. If plots make linear curve, it means it matches the theory. Depending on the index number n the plot becomes convex or concave curve. Index number that makes best linearity should be selected. There is a method that select positive number so that linearity becomes good since there is an idea that Index number n of DA method does not have to be limited to integral number in theory.

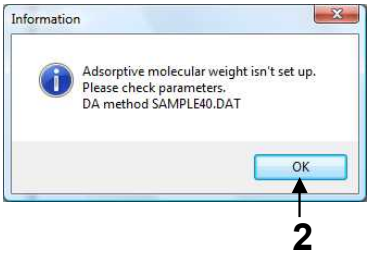
«Reference»

- "Theory of Volume Filling for Vapor Adsorption", B. P. Bering, M. M. Dubinin, and V. V. Serpinsky, *J. Colloid Interface Sci.,* 21, 378 (1966).

22-2. Operation

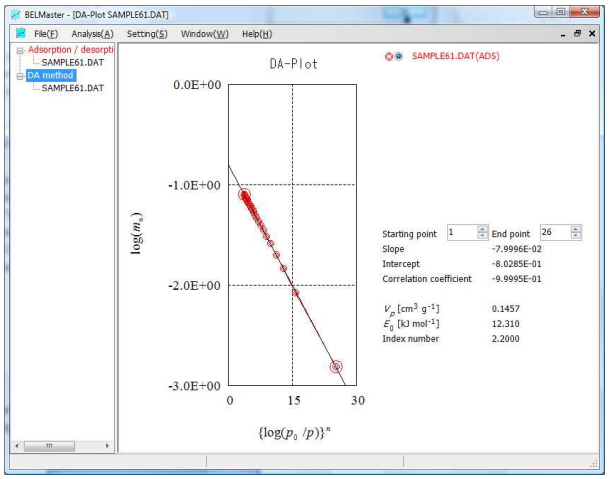
1. On the “Analysis (A)” menu, select “DA plot” and the screen will show the following DA plot windows. The program will execute a DA plot from the adsrotption data of an isotherm.

2. If no adsorbate molecular weight has been entered, the window shown on the right will appear. Click on the [OK] button and the analysis parameter window will open. Enter an adsorbate molecular weight (→ 6.).



3. A regression line is drawn between the 1st point and the last point. If the “Index number” is not appropriate, the linearity will decrease. Open the “Analysis parameter” window by selecting “Settings” and then the “Analysis parameters” menu. Then, enter an appropriate “Index number”.

4. Select the starting and end points of a straight line. The program will calculate pore volume (V_p/cm^3 g^{-1}) and adsorption potential (E_0/kJ mol^{-1})using the slope and intercept of this straight line. The m_a of y axsis (*log (m_a)*) as shown right figure is specific mass adsorbed on 1 g adsorbent.



V_p/cm^3 g^{-1} expressed as follows.

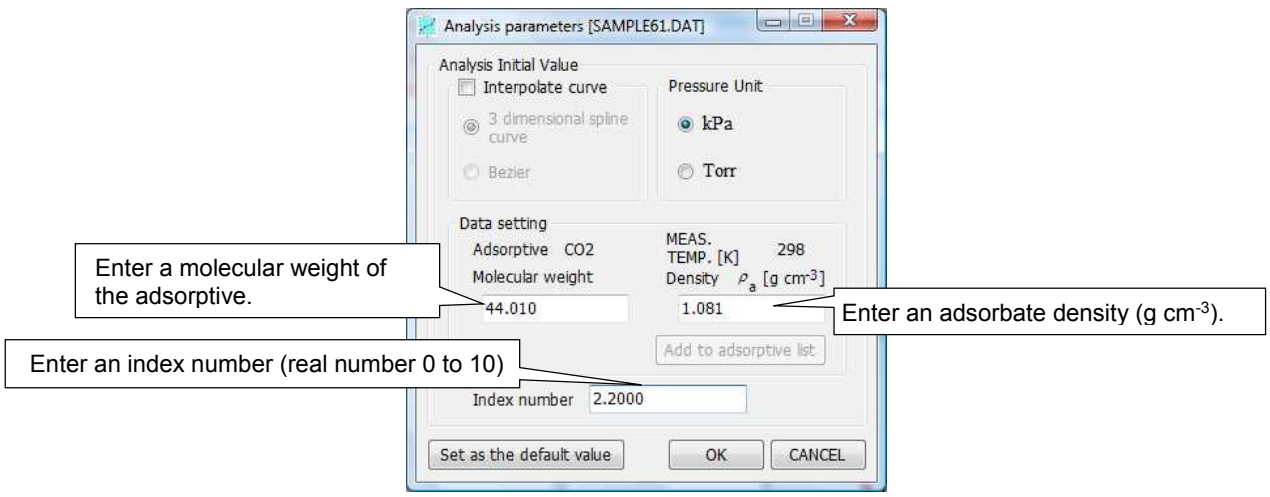
$$V = \frac{m_a}{\rho_a}$$

$$V_p = \frac{10^i}{\rho_a}$$

where ρa is anadsorbate density, i is the slope of straight line.

5. The figure on the right shows a DA-plot of carbon dioxide adsorption isotherm for microporous activated carbon. After entering an “index number” of 2.2, good linearity was obtained. The pore volume 0.146 cm^3 g^{-1} and adsorption potential 12.3 kJ mol^{-1} were obtained from the slope and intercept.

6. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown below will appear. Change the settings as needed. For details about items not described, see “7-1. Analysis parameters” on page 37.



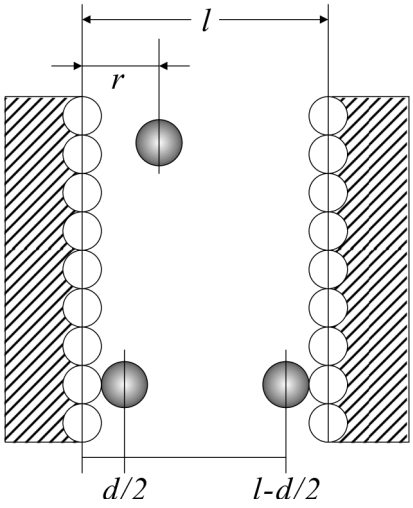
Chapter 23: HK plot

23-1. Description

There are a number of analysis methods suggested for drawing pore size distribution curve from adsorption isotherm, and most of them include a process to seek the relationship between pressure and pore size. For example, in BJH method, CI method and DH method, a relative pressure and filled pore size at the relative pressure are calculated by Kelvin equation. HK method introduced by Horvath and Kawazoe in 1983 calculates these values from average potential inside pores.

Suppose the distance between molecules is r, repulsive force occurs when the distance r is substantially short and attracting force occurs when it is a proper distance, and it can be ignored when the distance is large. The following equation is called Lennard-Jones potential, which regards potential energy U as a function of r.

$$U = C_m r^m - C_n r^n \tag{23.1}$$



C_m and C_n are constant numbers, and the first term of the right side of the equation indicates repulsive force and the second term indicates attracting force. The distance between one side of the pore surface and the other side is expressed by l as shown in the left diagram. The potential ϕ that the molecule at distance r away from the surface receives can be expressed as follows using 10:4 potential (m=10, n=4).

$$\phi = \frac{N_s A_s + N_a A_a}{2\sigma^4}\left[-\left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{l-r}\right)^4 + \left(\frac{\sigma}{l-r}\right)^{10}\right] \tag{23.2}$$

N_s indicates the number of atom per adsorbent unit surface area, and N_a indicates the number of molecule per unit surface area of adsorbate (already adsorbed). A_s and A_a are constant numbers that are determined by combination of adsorptive and adsorbent. Therefore, when the slit-shaped pore which has the distance *l* between the surfaces is filled the average potential energy can be expressed as follows.

$$\bar{\phi} = \frac{N_s A_s + N_a A_a}{2\sigma^4 (l-d)} \times \int_{d/2}^{l-d/2}\left[-\left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{l-r}\right)^4 + \left(\frac{\sigma}{l-r}\right)^{10}\right] dr \tag{23.3}$$

On the other hand, from the thermodynamic point of view, energy required for 1 mol gas adsorption is as follows.

$$\varepsilon = RT \ln(p_0 / p) \tag{23.4}$$

L=Avogadro constant, from equation (23.3) and (23.4),

$$RT\ln(p/p_0) = L\frac{N_s A_s + N_a A_a}{2\sigma^4(l-d)}\times \int_{d/2}^{l-d/2}\left[-\left(\frac{\sigma}{r}\right)^4+\left(\frac{\sigma}{r}\right)^{10}-\left(\frac{\sigma}{l-r}\right)^4+\left(\frac{\sigma}{l-r}\right)^{10}\right]dr \quad (23.5)$$

After integration, the following equation, which shows the relation between l and p, can be derived.

$$RT\ln(p/p_0) = L\frac{N_s A_s + N_a A_a}{\sigma^4(l-d)}\times \left[\frac{\sigma^4}{3(l-d/2)^3}-\frac{\sigma^{10}}{9(l-d/2)^9}-\frac{\sigma^4}{3(d/2)^3}+\frac{\sigma^{10}}{9(d/2)^9}\right] \quad (23.6)$$

HK method was invented in order to calculate pore size distribution of active carbon from nitrogen adsorption isotherm. Entering physicality values, it comes out as follows.

$$\ln(p/p_0) = \frac{62.38}{l-0.64}\times \left[\frac{1.895\times10^{-3}}{(l-0.32)^3}-\frac{2.7087\times10^{-7}}{(l-0.32)^9}-0.05014\right] \quad (23.7)$$

In BELSORP analysis software, pore size is determined at first, and then corresponding relative pressure is calculated. Then, adsorption amount at the relative pressure is worked out from linear interpolation of adsorption data, and integral curve can be obtained by plotting the adsorption amount against pore size. Pore size distribution curve can be drawn by differentiating integral curve.

As mentioned above, pore size distribution of active carbon is obtained from nitrogen adsorption isotherm, but in case of zeolite, this theory cannot be formed because interaction between cation inside pores and quadrupole momentum of nitrogen molecule is too strong. Emig *et al.* introduced coefficient for pore size distribution analysis of zeolite using argon adsorption isotherm, and it became common for zeolite analysis.

HK method is not suitable for analysis of pores that can cause capillary condensation because this method is based on adsorption potential theory. It is recommended to use low pressure range (relative pressure range below 0.05) for analysis.

HK plot

«Reference»

- "Method for the Caluculation of Effective Pore Size Distribution in Molecular Sieve Carbon", Géza Horváth and Kunitaro Kawazoe, *J.Chem.Eng.Japan*, 16, 470 (1983).

Table1 Physical Parameters for Micropore Size Calculation (**ISO 15901-3**)

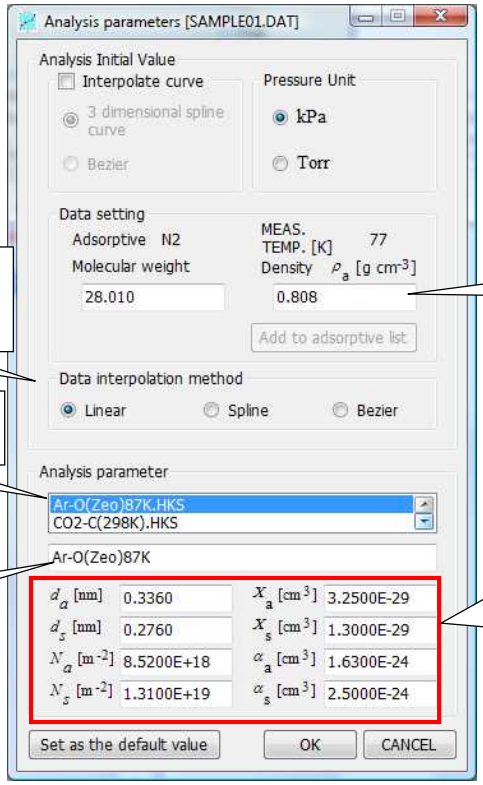
Physical quantity	Adsorbent parameters		Adsorptive parameters		
	Carbon	Zeolite	Nitrogen	Argon	Carbon dioxide
Diameter (nm)	0.34	0.28	0.30	0.34	0.40[1)]
Polarizability α (cm^3)	1.02 x 10^{-24}	2.50 x 10^{-24}	1.46 x 10^{-24}	1.63 x 10^{-24}	2.91 x 10^{-24} [2)]
Magnetic susceptibility χ (cm^3)※	13.5 x 10^{-29}	1.30 x 10^{-29}	2.00 x 10^{-29}	3.25 x 10^{-29}	3.49 x 10^{-29} [2)]
Density N (molecules m^{-2})	3.84 x 10^{19}	1.31 x 10^{19}	6.70 x 10^{18}	8.52 x 10^{18}	4.63 x 10^{18} [3)]

1) K. Kutics, G. Horvath, *Determination of Pore size distribution in MSC from Carbon-dioxide Adsorpton Isoterms*, **86**.
2) HANDBOOK OF CHEMISTRY AND PHSICS, 69th Edition, CRCPress, Inc.
3) Sicence of adsorption 2nd edition, Seiichi KONDOU, Tatuo ISHIKAWA, Ikuo ABE, Maruzen Co., LTD.

Operation

1. Select “HK plot” on the “Analysis (A)” menu and the screen will show the following HK plot window. The program will execute a HK plot from adsorption data of an isotherm.

2. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown below will appear. Change the settings as needed. Parameters saved as “Ar-O(87K) HKS,” “CO2-C(298K).HKS,” “N2-C(77K).HKS” cannot be changed. Change the name of the file displayed and then you can change the settings. Click on the [OK] button. The file will be stored as a new settings file. For details about items not described here, see section 7-1. “Analysis parameters,” on page 37.



Selectable an interpolation method to use for interpolating the analysis data.

If the parameters are already stored, select them from here.

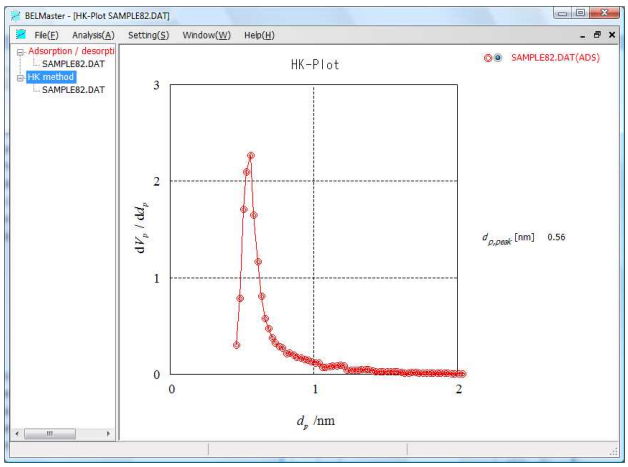
The currently selected parameter filename is displayed.

Enter a molecular weight and a density for the adsorbate.

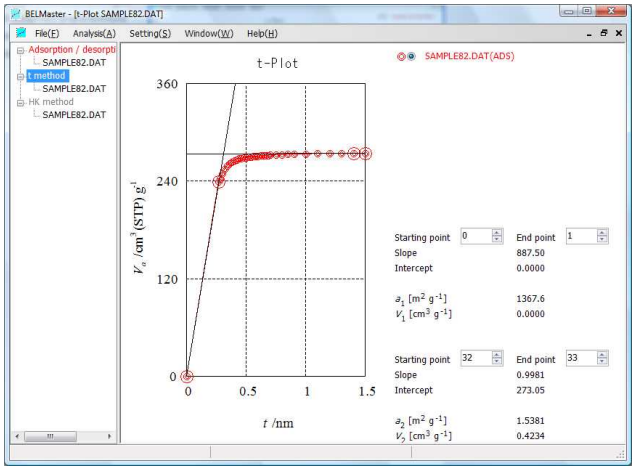
Enter parameters such as the molecular size and magnetic susceptibility. For details about each parameter, see the table below or the respective description.

Parameter		Unit
d_a	Adsorbate molecular diameter	nm
d_s	Adsorbent atom diameter	nm
N_a	Number of adsorbate molecules adsorbed per unit surface area	molecules m^{-2}
N_s	Number of adsorbent atoms per unit surface area	molecules m^{-2}
X_a	Magnetic susceptibility of the adsorbate molecular	cm^3
X_s	Magnetic susceptibility of the adsorbent atom	cm^3
α_a	Polarizability of the adsorbate molecules	cm^3
α_s	Polarizability of the adsorbent atoms	cm^3

3. The program will execute an HK plot using the specified conditions and will display the HK plot results. The figure on the right is an HK-plot measuring nitrogen adsorption by microporous activated carbon. It can be seen that this activated carbon has a large number of micropores 0.4 to 0.7 nm in width (d_p) and a distribution peak of 0.56 nm.



4. From the t plot of activated carbon shown on the right, the 1st straight line cannot be obtained and therefore the pore width cannot be given. This means that HK method is effective for activated carbon with pores 0.7 nm or less in width.



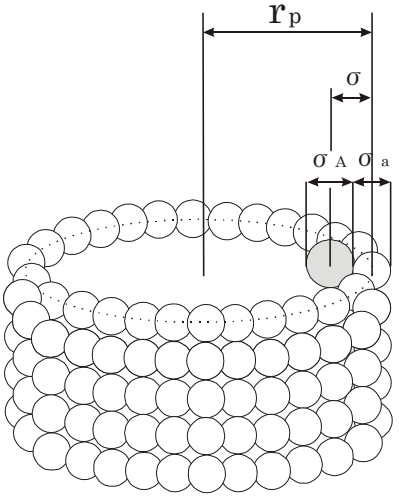
Chapter 24: SF plot

24-1. Description

As mentioned in Chapter 23 HK method analysis, for carbonaceous slit-shaped microporous materials such as active carbon, Horvath and Kawazoe made it possible to calculate micropore distribution by deriving the equation (23.7) of Chapter 23 from Hill's view[1)] of the average potential of N_2 molecule in micorpore.

Saito and Foley applied this idea of average potential to cylinder-shaped micropore using Everett and Powl's view of potential[2)], and succeeded to calculate micropore distribution of zeolite, $AlPO_4$ and etc[3)4)].

There are 2 different ideas for taking the potential inside cylinder-shaped micropore. One is line average model and the other is area average model. In line average model, molecules have only one degree of freedom, which is along the diameter of micropore. On the other hand in area average model, the molecules have two degree of freedom to move across the micorpore. It is proved from some actual analysis that area average model corresponds to crystallographic view. BEL Japan analysis software also uses area average model.



If the above mentioned "area average model" is used, the following formula is derived, which is corresponding to the formula (23.6) of Chapter 23.

$$\ln(P/P0) = \frac{3}{4}\frac{\pi L}{RT}\frac{(N_s A_s + N_a A_a)}{\sigma^4}\times \sum_{k=0}^{\infty}\left[\frac{1}{k+1}\left(1-\frac{\sigma}{r_p}\right)^{2k}\left\{\frac{21}{32}\alpha_k\left(\frac{\sigma}{r_p}\right)^{10}-\beta_k\left(\frac{\sigma}{r_p}\right)^{4}\right\}\right] \quad (24.1)$$

α_k and β_k are indicated Γ function and calculated from the following formulas.

$$\alpha_k^{0.5} = \frac{\Gamma(-4.5)}{\Gamma(-4.5-k)\Gamma(k+1)}$$

$$\beta_k^{0.5} = \frac{\Gamma(-1.5)}{\Gamma(-1.5-k)\Gamma(k+1)}$$

Please refer to HK method analysis (Chapter 22) for N_s, A_s, N_a and A_a that are used in the formulas.

In case of zeolite or $AlPO_4$, surface atoms are considered to be oxygen atoms. In case of N_2 adsorption in this type of system, it is difficult to make accurate adsorption isotherms because quadrupole momentum of N_2 molecule and solid surface atom cause specific interaction. Therefore, in case of oxide microporous material, Ar, which is mono-atomic molecule, is generally used as the adsorption molecule. Ar has boiling point of 87 K and the molecular size of 0.336 nm (molecular diameter), and it can be handled almost in the same manner as for N_2. Therefore, the parameters necessary for the calculation of N_s, A_s, N_a and A_a of (24.1) are as indicated in the table below.

Table 2 Physical Parameters for Micropore Size Calculation (ISO 15901-3)

Physical quantity	Adsorbent Oxide Ion	Adsorbate Argon
Diameter (nm)	0.28	0.34
Polarizability α (cm^3)	2.50×10^{-24}	1.63×10^{-24}
Magnetic susceptibility χ (cm^3)	a) 1.30×10^{-29} b) 1.9×10^{-29} 1)	3.25×10^{-29}
Density N (molecules cm^{-2})	1.31×10^{19}	8.52×10^{18}

1) A. Saito, H. C. Foley, *Microporous Materials*, **3** (1995) 531.

The following equation is derived from the calculation of each parameter of (24.1) based on Table 1.

$$\ln\left(\frac{p}{p_0}\right) = \varepsilon^* \sum_{k=0}^{\infty}\left[\frac{1}{k+1}\left(1-\frac{0.306}{r_p}\right)^{2k} \times \left\{\frac{21}{32}\alpha_k\left(\frac{0.306}{r_p}\right)^{10} - \beta_k\left(\frac{0.306}{r_p}\right)^{4}\right\}\right] \qquad (24.2)$$

where

$$\alpha_k = \left(\frac{-4.5-k}{k}\right)^2 \alpha_{k-1}$$

and

$$\beta_k = \left(\frac{-1.5-k}{k}\right)^2 \beta_{k-1}$$

ε^*, magnetic susceptibility value of oxygen, varies according to the choice between a) and b). It is 36.47 when a) is used, and 44.53 when b) is used. In practice, a) is used for ZSM-5 or Y type zeolite, and b) is used for $AlPO_4$.

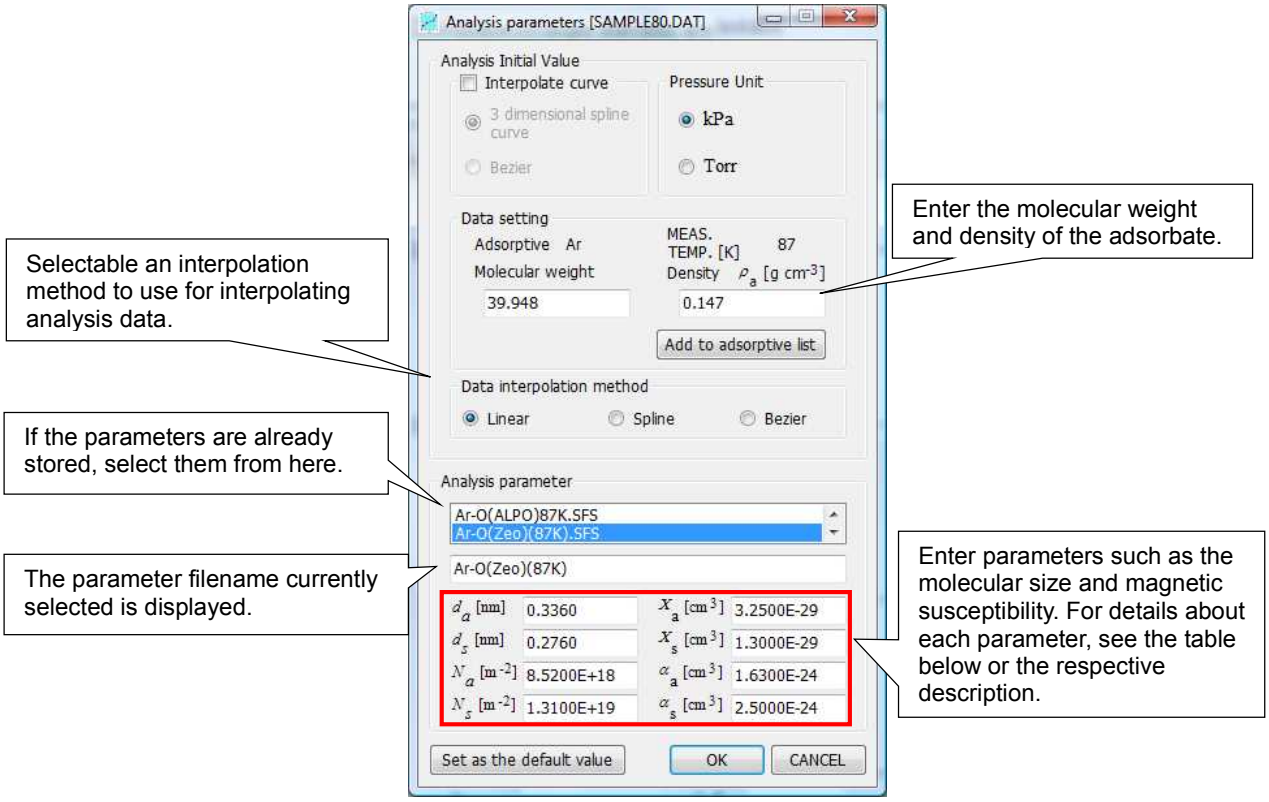
In micropore calculation, pore size is determined first, then relative pressure respect to the pore size is calculated using the equation (24.2). Integral curve can be obtained by calculating the adsorption amount against relative pressure that is obtained from (24.2) by interpolation equation using the adsorption data of the adsorption isotherm, and then plotting adsorption amount versus pore size. Pore size distribution curve can be obtained by differentiating this integral curve.

«Reference»
1) T.L.Hill ,*J.Chem.Phys*., **17**, 590 (1949).
2) D.H.Everett, J.C.Powl, *J.Chem.Soc., Faraday Trans. 1*,**72**,619 (1976).
3) A.Saito, H.Foley, *AIChE J*., **37**, 429 (1991).
4) A.Saito, H.Foley *Microporous Material*, **3**, 531 (1995).

24-2. Operaion

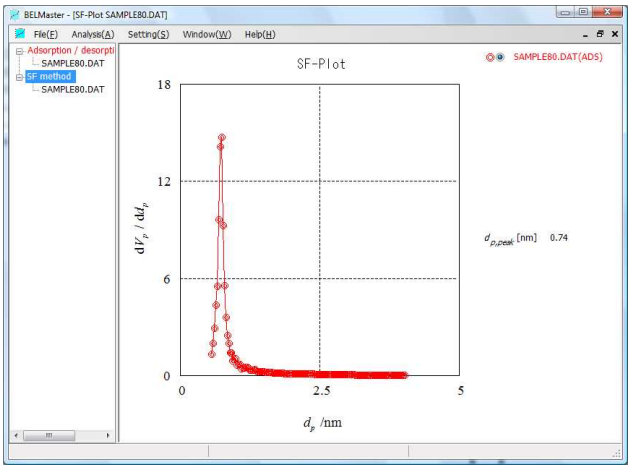
1. On the “Analysis (A)” menu, select “SF plot” and the screen will show the following SF plot windows. The program will execute an SF plot from adsorption data of an isotherm.

2. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown below will appear. Change the settings as needed. Parameters saved as “Ar-O(87K) SFS” and “Ar-O(Zeo)87K.SFS” cannot be changed. Change the name of the file being displayed and then you can change the settings. Click on the [OK] button. The file will be saved as a new settings file. For details about items not described here, see section 7-1. “Analysis parameters,” on page 37.



		Unit
d_a	Adsorbate molecular diameter	nm
d_s	Adsorbent atom diameter	nm
N_a	Number of adsorbate molecules adsorbed per unit surface area	molecules m^{-2}
N_s	Number of adsorbent atoms per unit surface area	molecules m^{-2}
X_a	Magnetic susceptibility of the adsorbate molecules	cm^3
X_s	Magnetic susceptibility of the adsorbent atoms	cm^3
α_a	Polarizability of the adsorbate molecules	cm^3
α_s	Polarizability of the adsorbent atoms	cm^3

3. The program will execute an SF plot using the specified conditions and will display the SF plot results. The figure on the right is an SF-plot of an argon isotherm for microporous zeolite. It can be seen that this zeolite has a large number of micropores 0.5 to 0.9 nm in width (d_p), and a distribution peak at 0.74 nm.



Chapter 25: Isosteric heat of adsorption

25-1. Description

Adsorption involves heat generation. It is important to measure this heat quantity for studying surface area characteristics.

When gas adsorption happens under constant temperature, heat of $\mathrm{d}Q$ is created. q_{diff} which is expressed by the following equation is called differential heat of adsorption.

$$q_{diff} = \frac{\mathrm{d}Q}{\mathrm{d}n_a} \tag{25.1}$$

Heat quantity produced at adsorption is so small, and it is difficult to measure. Therefore, isosteric heat of adsorption is calculated with the following theory.

The following relation comes in effect at adsorption equilibrium.

$$G_a = G_g \tag{25.2}$$

G indicates free energy of Gibbs, and a and g indicate adsorbate (adsorption molecules that are adsorbed) and adsorptive (adsorption molecules in gaseous phase) respectively. Suppose there is no change in adsorption amount n_a and only adsorption temperature changes. Change of free energy can be expressed as the following:

$$\mathrm{d}G_g = -S_g \mathrm{d}T + V_g \mathrm{d}P \tag{25.3}$$
$$\mathrm{d}G_a = -S_a \mathrm{d}T + V_a \mathrm{d}P \tag{25.4}$$

n_a is constant, thus

$$\mathrm{d}G_a = dG_g \tag{25.5}$$

The following equation can be derived from (25.2), (25.3) and (25.4)

$$\left(\frac{\partial P}{\partial T}\right)_{n_a} = \frac{S_g - S_a}{V_g - V_a} \tag{25.6}$$

Applying $V_g=RT/P$ ($V_g \gg V_a$) from the state equation of ideal gas, the above equation becomes as follows.

$$\left(\frac{\partial \ln P}{\partial T}\right)_{n_a} = (S_g - S_a)RT = -\Delta S_{ads} / RT \tag{25.7}$$

Suppose $S_g - S_a = \Delta S_{ads}$. At equilibrium state, enthalpy change caused by adsorption ΔH_{ads} has the following relation with absolute temperature and entropy.

$$\Delta H_{ads} = T\Delta S_{ads} \tag{25.8}$$

Following equation can be obtained from (25.6).

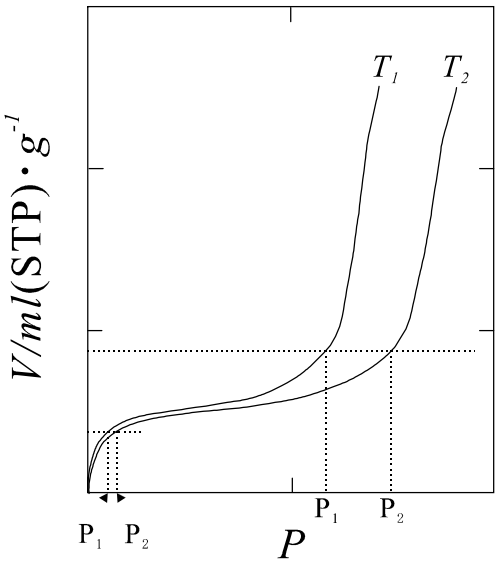
$$\left(\frac{\partial \ln P}{\partial T}\right)_{n_a} = -\frac{\Delta H_{ads}}{RT^2} = \frac{q_{st}}{RT^2} \tag{25.9}$$

$-\Delta H_{ads}$ is differential enthalpies of adsorption q_{st}. The relation between q_{st} and q_{diff} is as follows.

$$q_{st} = q_{diff} + RT \tag{25.10}$$

The process to calculate adsorption heat from Clausius-Clapeyron equation is as follows. At least 2 different adsorption isotherms that were measured at different temperatures T_1 and T_2 are needed for the analysis. The BEL Master software enables analysis with two or three adsorption isotherms. q_{st} at an adsorption amount can be calculated from the equation below with the difference between the 2 different pressures at the same adsorption amount (Refer to the graph below) .

$$q_{st} = \frac{RT_1T_2}{T_2 - T_1}(\ln p_2 - \ln p_1) \tag{25.11}$$

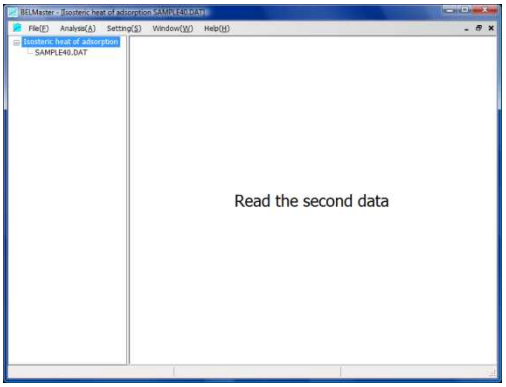


Heat of adsorption is closer to heat of condensation where adsorption amount is large. Heat of adsorption at low adsorption amount is important for the surface characteristic study. However, in the method that uses Clausius-Clapeyron equation, the difference in pressures is so small at low adsorption that error becomes large. Also, this equation can be formed only for reversible reaction, thus it is impossible to calculate heat of chemical adsorption etc.

25-2.

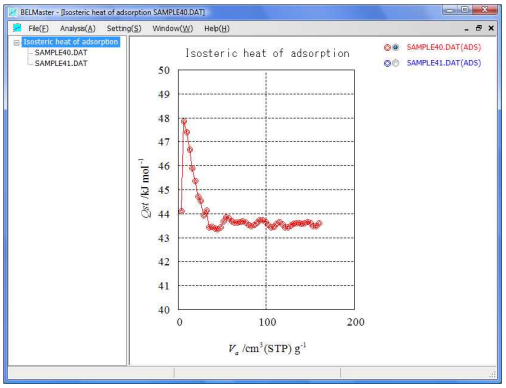
25-2. Operation

1. The program will execute an isosteric heat of adsorption analysis from adsorption data of the isotherm. This analysis reads two data files measured at different adsorption temperatures. Select “Isosteric heat of adsorption” on the “Analysis (A)” menu and read the first set of data. The screen will display “Read the second data”.

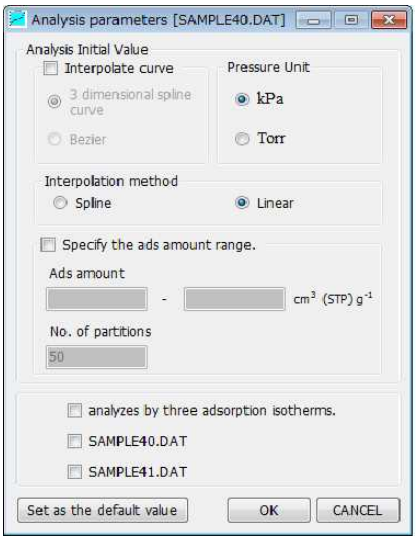


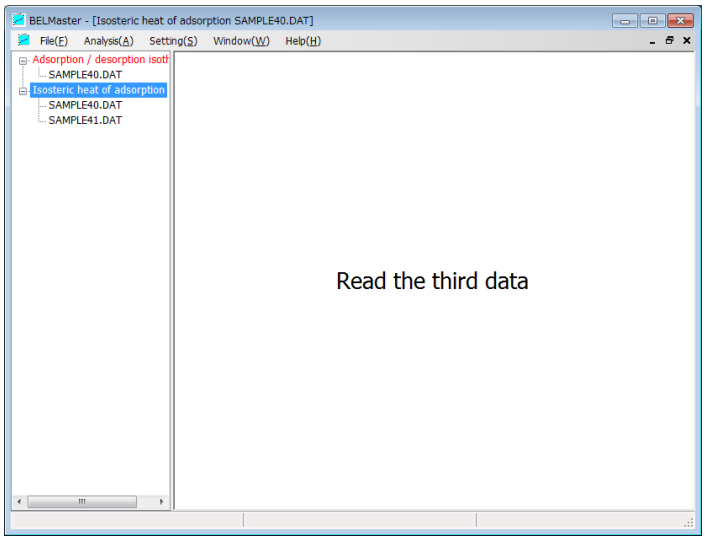
2. On the BEL analysis program menu, or the menu displayed by clicking the mouse right button, select “Read additional data” and then read the 2nd set of data.

3. Obtain the isosteric heat of adsorption from these two sets of data. The figure on the right is the result of adsorption of water vapor on non-porous silica.



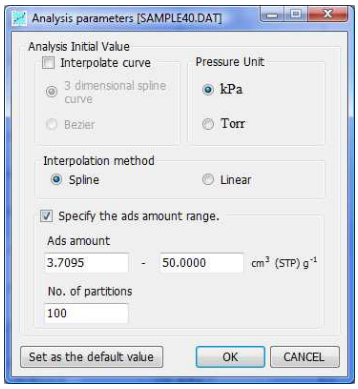
To execute analysis with three isotherms, select [Read additional data] in the analysis software menu, or in the sub window right-click menu, and read data on the third isotherm. Also, selecting [Analysis with three adsorption isotherms] in [Analysis parameters] enables analysis with three isotherms.



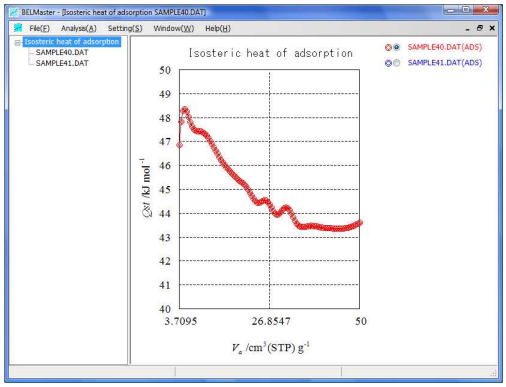


4. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown right will appear. Change the settings as needed.

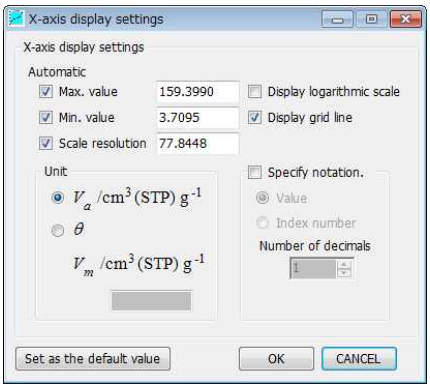
   When “Specify the ads amount range” is selected, the program will calculate the Isosteric heat of adsorption specified in the table below (“ads amount” and “No.of partitions (5 ≤ “No. of partitions ≤ 500)).



5. The figure on the right is the result of isosteric heat of adsorption specified ads amount (3.7095-50.000 cm^3 (STP)g^{-1}) and No. of partitions (100).



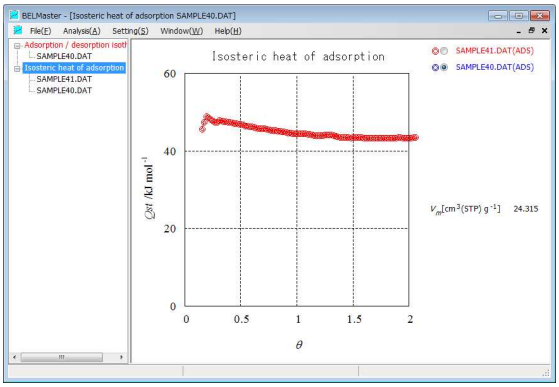
6. For analysis of isosterioc heat of adsorption, “*Va/cm³ (STP) g⁻¹*” or “*θ*” can be selected for the X-axis unit in [Setting] – [X-axis setting].



“*Va/cm³ (STP) g⁻¹*” Indicates adsorption volume.
“*θ*” Indicates surface coverage.

Enter monomolecular adsorption volume *Vm/cm³ (STP) g⁻¹*. Monomolecular adsorption volume can be obtained by BET analysis.

7. The right graph shows a result of isosterioc heat of adsorption, wherein surface coverage is plotted on the X-axis.



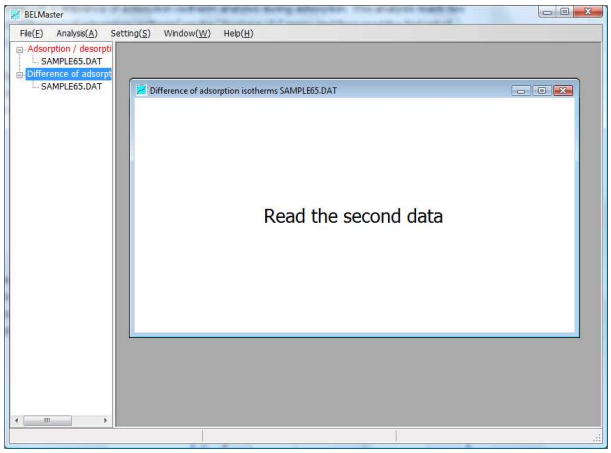
Chapter 26: Difference of adsorption isotherm

26-1. Description

The diffirence between two isotherms can be obtained with this analysis. This is a useful method for analysis of chemical adsorption amount.

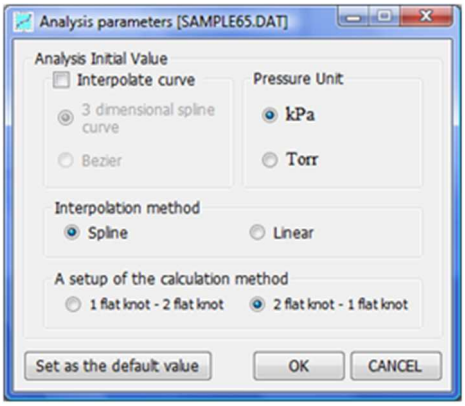
26-2. Operation

1. The program will execute a difference of adsorption isotherm analysis during adsorption. This analysis reads two isotherms. Select “difference of adsorption isotherm” on the “Analysis (A)” menu and then read the first set of data. The screen will display “Read the second data”.

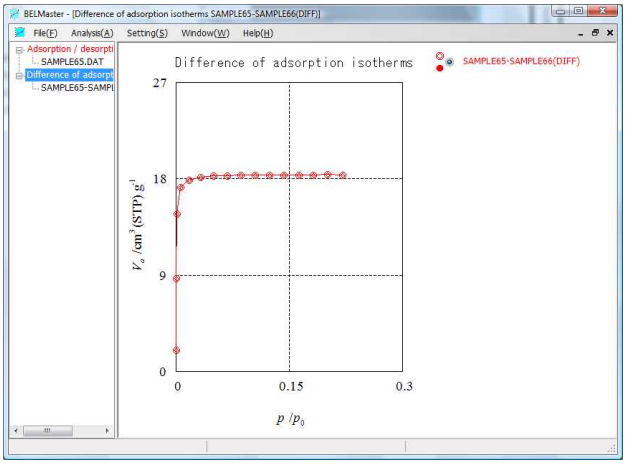


2. On the BEL analysis program menu, or the menu displayed by clicking the mouse right button, select “Read additional data” and then read the 2nd set of data.

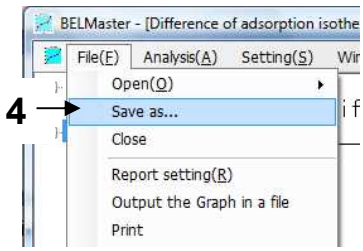
3. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown on the right will appear. Change the settings as needed.



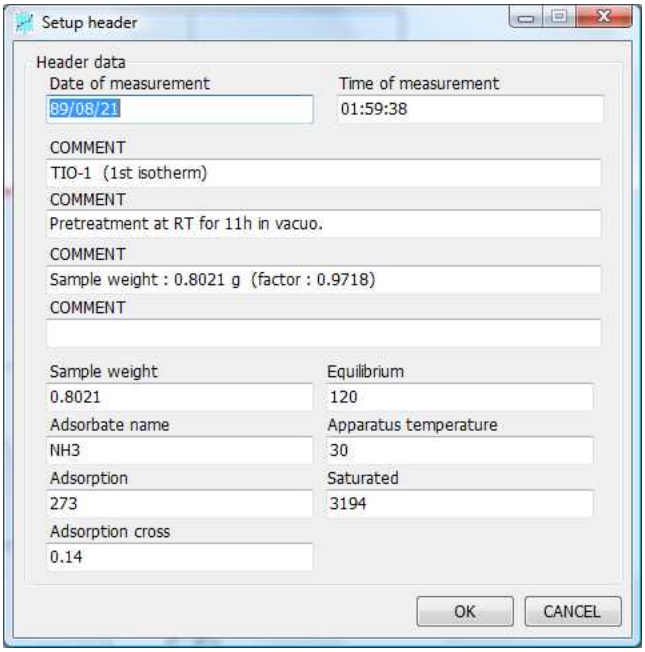
4. Obtain the difference of adsorption isotherm from these two sets of data. The program obtains the adsorption volume of the 2nd set of data by interpolating it with the relative pressure from the 1st set of data. The figure on the right is the result of measuring ammonia adsorption (1st and 2nd adsorption trials) by titanium oxide. The chemical adsorption of ammonia by titanium oxide can be calculated as 18.4 $cm^3(STP)g^{-1}$.



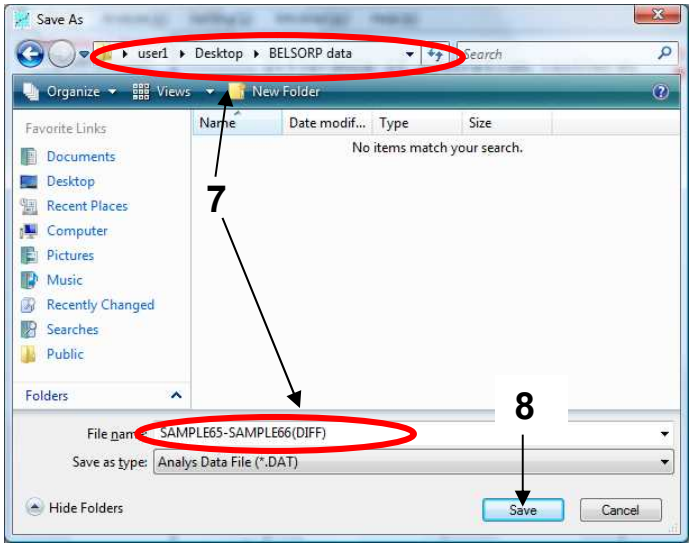
5. The data obtained from a “difference of adsorption isotherms” can be saved in an “adsorption isotherm” file. The data can later be analyzed using other analysis methods like a Langmuir plot. To save a difference of adsorption isotherm, select “File (F),” and then “Save as”.



6. The “Setup header” window shown on the right will appear. Sample information items are displayed for 1st set of data read. After entering information concerning the difference of adsorption isotherm data you want to save, click on the [OK] button.



7. Specify a location to save the file and enter a filename in the “Save As” window.



8. Click on the [Save] button and the program will save the data.

9. The data can be analyzed later by selecting “File (F),” “Open (O),” and then the (analysis name).
In the example above, the program analyzes the saved “difference of adsorption isotherm” using a Langmuir analysis, and calculates the volume of ammonia chemically adsorbed by titanium oxide.

Chapter 27: Metal dispersion analysis

27-1. Description

Metal dispersion can be calculated from gas adsorption amount (chemical adsorption amount) as follows. Adsorption amount value used in this calculation is given as gas volume of standard condition V[ml(STP) g^{-1}].

N_g, the number of moles of the gas that adsorobed on supported metal catalyst 1 g is expressed as bellow.

$$N_g = \frac{V}{22414} \tag{27.1}$$

The metal atoms that has gas adsorption on the surface, in other words, the number of moles of the metal atoms that are exposed on the catalyst surface is represented as follows (Stoichiometry factor=k_{sf}).

$$N_s = k_{sf} \times N_g = k_{sf} \times \frac{V}{22414} \tag{27.2}$$

wt% of metal loading is *c*%. The number of moles of metal atom per catalyst 1 g , N_T , can be calculated from the following equation.

$$N_T = \frac{c}{M} \times \frac{1}{100} \tag{27.3}$$

Here, M indicates atomic weight of supported metal atom.

Therefore, metal dispersion rate D_m can be calculated by the following equation.

$$D_m = \frac{N_s}{N_T} = k_{sf} \times \frac{V}{22414} \times \frac{M \times 100}{c} \tag{27.4}$$

a_s(*Sample*) [m^2·g^{-1}], supported metal surface area per catalyst 1 g can be calculated by the following.

$$a_s(Sample) = \frac{k_{sf} \times V \times 6.022 \times 10^{23}}{22414} \times a_m \times 10^{-18} \tag{27.5}$$

Also a_s(*Metal*) [m^2·g^{-1}], supported metal surface area per supported metal 1 g can be calculated by the following.

$$a_s(Metal) = \frac{a_s(Sample) \times 100}{c} \tag{27.6}$$

a_m[nm^2 atom^{-1}] is the cross section area that a supported metal atom occupies (supported metal cross section area).

Suppose supported metal particle is cubic, the particle size l_m[nm] is,

$$l_m = \frac{6}{\rho \times a_s(Metal)} \times 10^3 \tag{27.7}$$

where ρ[cm^3 g^{-1}] is the density of supported metal.

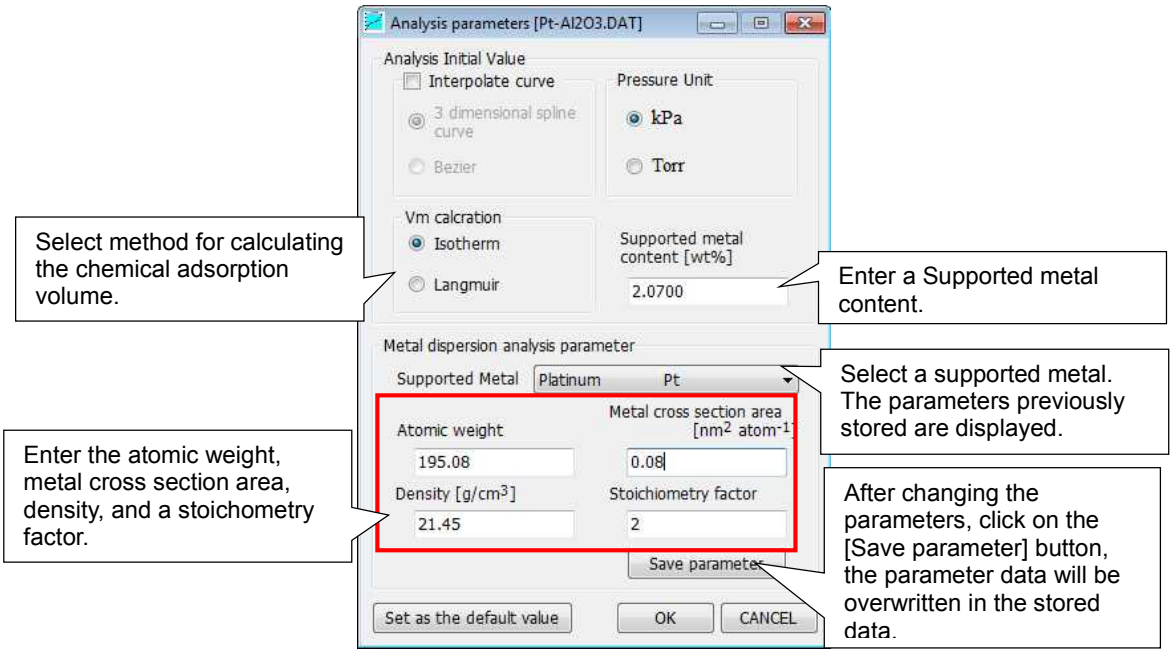
There are various ways to evaluate cross-sectional area of supported metal, and many values are listed in literatures. The following table indicates some examples that were calculated from average surface atom concentration, which are described in a literature (Catalyst course(additional volume), Catalyst experiment handbook, P261).

Supported metal		Atomic weight	Density/g·cm^{-3}	Metal cross section area/ nm^2·atom^{-1}
Iron	Fe	55.847	7.87	0.0613
Cobalt	Co	58.933	8.90	0.0662
Nickel	Ni	58.690	8.90	0.0649
Copper	Cu	63.546	8.96	0.0680
Molybdenum	Mo	95.940	10.22	0.0730
Ruthenium	Ru	101.070	12.41	0.0613
Rhodium	Rh	102.906	12.41	0.0752
Palladium	Pd	106.420	12.02	0.0787
Argentum	Ag	107.868	10.50	0.0870
Rhenium	Re	186.207	21.01	0.0649
Iridium	Ir	192.220	22.42	0.0769
Platinum	Pt	195.080	21.45	0.0800

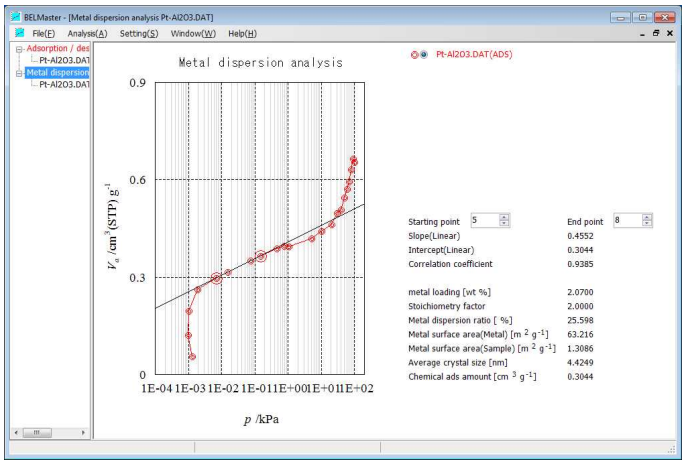
27-2. Operation

1. Select “Metal dispersion analysis” on the “Analysis (A)” menu and the following metal dispersion analysis windows will be displayed. The program will execute a metal dispersion analysis from adsorption data of isotherms.

2. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown below will appear. Change the settings as needed. For details about items not described here, see section 7-1. “Analysis parameters,” on page 37.



3. Select the starting and end points of an approximate curve. The metal loading (%), stoichometry factor, inclination of the approximate curve, slice, correlation coefficient, metal distribution ratio (%), metal surface area (Metal) (m^2 g^{-1}), metal surface area (Sample) (m^2 g^{-1}), metal powder diameter (nm), average crystal size (nm), and chemical adsorption volume (cm^3 g^{-1}) will be displayed.

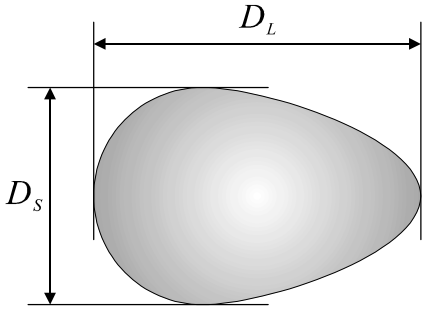


Chapter 28: Molecular probe method

28-1. Description

In case of adsorbent with very small pores, it is difficult to calculate pore from nitrogen adsorption isotherm. Molecular probe method is a method used in cases like this that produces adsorption isotherm using some adsorbates with different molecular size, and then measures distribution from the relationship between molecular size and pore volume. There are four materials that are often used as the probe. They are CO_2, C_2H_6, n-C_4H_{10} and iso-C_4H_{10} in ascending order. Naturally, adsorptives larger than a pore cannot enter the pore. Therefore, bigger the adsorption molecule is smaller the pore volume can be obtained from the isotherm. Measurement of isotherm is preceded from smaller adsorbates to bigger ones and pore volume W_0 is worked out by DA method. If W_0 becomes almost zero sebsequent adsorption measurements does not have to be carried out. Using non-linear least squares method, Gaussian distribution is optimized and integral curve is calculated taking each adsorbate size in X-axis and W_0 in Y-axis.

Molecular probe method is considered to be one of the most accurate analysis methods because it measures distribution by inspecting whether molecules can enter pores. However, it takes lots of time and work as it needs more than one adsorption isotherms to produce one pore distribution curve. Adsorbate that does not cause chemical adsorption has to be selected for the probe. Molecular size depends on molecular model. Minor axis length D_S of smallest projection cross section area in case of slit-shaped pore, and major axis length D_L of smallest projection cross section area in case of cyrinder-shaped pore, are used (Refer to the right diagram.).

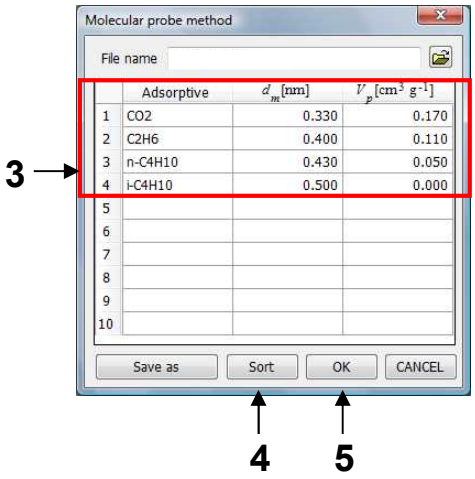


28-2.

28-2. Operation

1. Using adsorption isotherms from some types of adsorbates with different molecular diameters, calculate the pore volume using a DA or other plot.

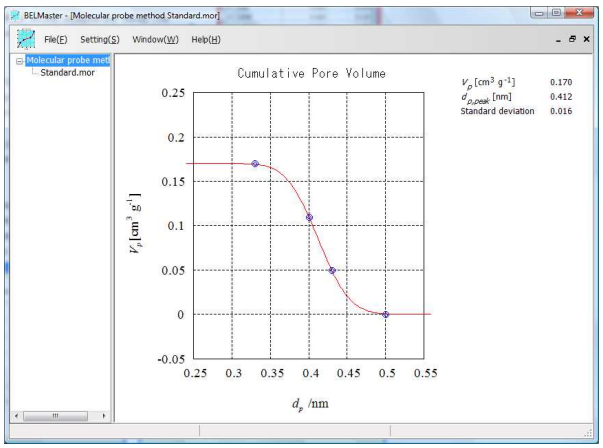
2. Select a “Molecular probe method” on the “Analysis (A)” menu. The “Molecular probe method” numerical data window shown below will appear.

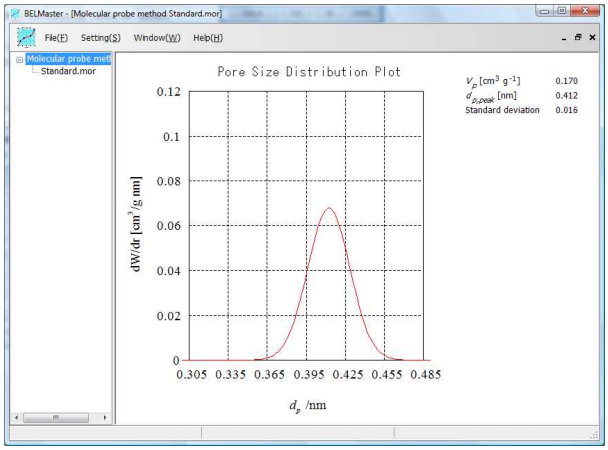


3. Enter an “Adsorbate name,” “d_m (adsorbate molecular diameter),” and “V_p (pore volume)”. If molecular probe analysis data is already stored, click  and you can select a file. Change the numerical values as needed.

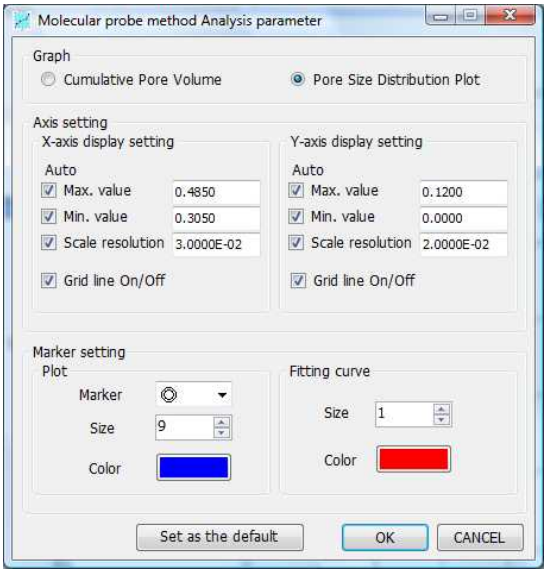
4. Click on the [Sort] button, the program will sort data in order of larger to smaller d_m (adsorbate molecular diameter). Click on the [Save as] or [OK] button and the program will sort the data automatically.

5. After entering data, click on the [OK] button and the screen will display the “Cumulative Pore Volume” (lower left figure) or “Pore Size Distribution Plot” (lower right figure). The “Cumulative Pore Volume” is a graph plotting the pore volume (V_p / cm^3 g^{-1}) against the pore diameter (d_p/nm). The “Pore Size Distribution Plot” is a graph differentiating the “Cumulative Pore Volume”.

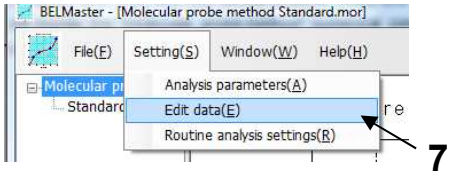




6. On the analysis menu, select “Setting” and “Analysis parameter,” the screen will show the “Molecular probe method Analysis parameter” window. You can select graph type, specify X and Y axes, and markers.

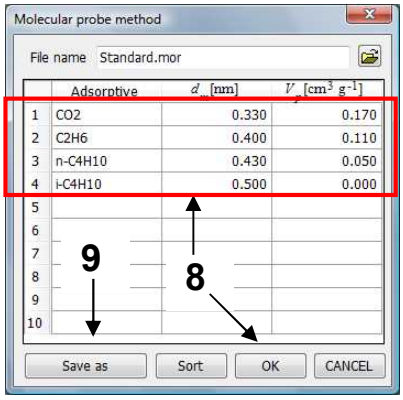


7. Select “Setting(S)” and “Edit data (E)” on the analysis menu and the program will display the “Molecular probe method” numerical data window. You can modify the molecular probe data in this window.



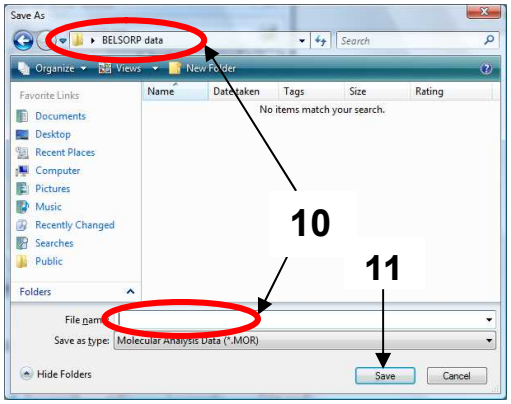
8. After changing the data, click on the [OK] button, and check the graph that is displayed.

9. Click on the [Save as] button in the “Molecular probe method” numerical data window and you can save the numerical data in a new file.



10. Specify a location to save the file and enter a filename.

11. Click on the [Save] button and the program will save the data in the molecular probe analysis data format: filename.mor



Chapter 29: NLDFT/GCMC method

29-1. Description

1) Introduction

The non-localized density functional theory (NLDFT: Non Localized Density Functional Theory) and the computer simulation method (GCMC: Grand Canonical Monte Carlo method) have been developed as new pore distribution evaluation methods for porous materials. Evans and Tarazon studied adsorption and phase of fluid in pores through molecular modeling based on DFT by using computers[1, 2]. After that, Seaton *et al.* studied calculation of pore distribution based on DFT[3]. The pore distribution analysis based on the initial DFT provided satisfactory results to discuss adsorption status in pores. However, it has a problem about quantitative measurement in micropores.

Then, to solve the problem about quantitative measurement, Latoskie, Gubbins and Quirke established the NLDFT method[4, 5]. This theory can explain adsorption phenomena of adsorptives into many materials, which can be applied to pore distribution analyses for micropores and mesopores[6].

Features of these theories are to execute analysis on the assumption that adsorption density will periodically change from solid surfaces, while classic pore distribution analysis theories are based on the assumption that adsorption occurs in liquid state (Kelvin theory). For the pore distribution calculation, it is absolutely necessary to select the pore structure (slit or cylindrical, cage), and to determine parameters related to adsorptive and adsorbent (N_2/Ar/CO_2, Carbon/Oxygen). By using these parameters, theoretical adsorption isotherms for various pore diameters can be obtained based on the NLDFT or GCMC method. Then, a pore distribution curve is calculated by fitting an integral isotherm obtained from the theoretical adsorption isotherms to the experimental isotherm so that an adsorption amount error can be minimized.

This new pore distribution evaluation method enables pore distribution analysis in the whole range with a single theory, although conventional evaluation methods use different theories individually to evaluate distribution of mesopores and micropores.

2) NLDFT

NLDFT has been developed in applications to classic studies of non-uniform fluids. For a simple fluid, this method can accurately express periodical changes in density from solid surface and fluid density relative to a defined pore structure (slit-shaped etc.). NLDFT can express such adsorption equilibrium in pores with a grand canonical ensemble system.

$$\Omega[\rho_L(r)] = F[\rho_L(r)] - \int \rho_L(r)[\mu - V_{ext}(r)]dr \qquad (29\text{-}1)$$

In the above equation, F is intrinsic Helmholts free energy function, ρ_L is fluid density localized at position r, and d is a (hard sphere) diameter. Calculation of $V_{ext}(r)$ is different depending on pore model. Details are described in the next section.

$$F[\rho_L(r)] = F_h[\rho_L(r);d] + \frac{1}{2}\int\int dr dr' \rho_L(r)\rho_L(r')\phi_{att}(|r-r'|) \qquad (29\text{-}2)$$

Gravitational force potential ϕ_{att} can be obtained with Weeks-Chandler-Anderson equation[5].

$$\phi_{att}(|r-r'|) = \phi_{ff}(|r-r'|), \quad \text{at} \quad |r-r'| > r_m \qquad (29\text{-}3)$$

$$= -\varepsilon_{ff}, \quad \text{at} \quad |r-r'| < r_m \qquad (29\text{-}4)$$

$$r_m = 2^{1/6}\sigma_{ff} \qquad (29\text{-}5)$$

The term for hard sphere (F_h) can be classified into the term for ideal gas (F_{id}) and the term of excess amount (F_{ex}).

$$F_h\left[\rho_L(r)\right] = F_{id}\left[\rho_L(r)\right] + F_{ex}\left[\rho_L(r);d\right] \quad (29\text{-}6)$$

$$F_{id}\left[\rho_L(r)\right] = kT\int dr\rho_L(r)\left[\ln\left(\Lambda^3\rho_L(r)\right)-1\right] \quad (29\text{-}7)$$

$\Lambda = h/(2\pi mkT)^{1/2}$ indicates de Broglie wave. m indicates molecular weight of adsorptive, and h and k are Planck's constant and Boltzmann constant, respectively.

$$F_{ex}\left[\rho_L(r);d\right] = kT\int dr\rho_L(r)f_{ex}\left[\bar{\rho}(r);d\right] \quad (29\text{-}8)$$

Helmholts free energy per molecule of hard sphere (f_{ex}) is expressed with the equation below.

$$f_{ex}\left[\bar{\rho}(r);d\right] = \mu_h\left[\bar{\rho};d\right] - \frac{P_h\left[\bar{\rho}(r);d\right]}{\bar{\rho}(r)} - kT\left[\ln\left(\Lambda^3\bar{\rho}(r)\right)-1\right] \quad (29\text{-}9)$$

In the above equation, μ_h and P_h indicate chemical potential and pressure respectively, which are calculated by Carnahan-Starling equation[1, 7].

$$P_{hd}\left[\bar{\rho}\right] = \bar{\rho}kT\frac{1+X+X^2+X^3}{(1-X)^3} \quad (29\text{-}10)$$

$$\mu_{hs}\left[\bar{\rho}\right] = kT\left[\ln\left(\Lambda^3\bar{\rho}\right)+\frac{8X-9X^2+3X^3}{(1-X)^3}\right] \quad (29\text{-}11)$$

$$X = \frac{\pi}{6}\bar{\rho}d^3 \quad (29\text{-}12)$$

In this step, NLDFT uses Tarazona theory of smoothed function to calculate density in adsorption phase[1, 2].
Θ : Heaviside step function

$$\bar{\rho}(r) = \int dr'\,\rho_L(r')w\left[|r-r'|;\bar{\rho}(r)\right] \quad (29\text{-}13)$$

$$w(r;\rho) = w_0(r)+w_1(r)\rho+w_2(r)\rho^2 \quad (29\text{-}14)$$

$$w_0(r) = \frac{3}{4\pi d^3}\Theta(d-r)$$

$$w_1(x) = \frac{6}{\pi}\left(a_0+a_1x+a_2x^2\right) \text{ at } x = r/d \le 1$$

$$w_1(x) = \frac{6}{\pi}\left\{ce^{-\beta_1(x-1)}\sin\left[\alpha(x-1)\right]+e^{-\beta_2(x-1)}\left(b_0+b_1x+b_2x^2+b_3x^3\right)\right\} \text{ at } x = r/d > 1$$

$$w_2(r) = \frac{5}{4\pi}\left(\frac{6}{\pi}\right)\left[6-12\frac{r}{d}+5\left(\frac{r}{d}\right)^2\right]\Theta(d-r)$$

As described above, density profile can be calculated. Then, density that provides minimum grand potential is calculated, and the calculation result is equilibrium state.

$$\frac{\delta\Omega\left[\rho_L(r)\right]}{\delta\rho_L(r)} = 0 \quad \text{at} \quad \rho_L = \rho_{L,eq} \quad (29\text{-}15)$$

To minimize energy, density is calculated with Lagrangian multiplier method[8].

Fig. 1 shows a density profile curve for a slit-shaped pore model (N_2, T=77 K, H=4.3 nm). In this figure, we can see that monomolecular layer adsorption starts at P/P_0 = 10^{-5}. According to an increase in relative pressure, the local density increases, and adsorption of the second layer starts at P/P_0 = 10^{-1}.

The periodical change in local density is gradually eliminated from the third and subsequent layers, and the density becomes close to the average density of the bulk. In view of this, it is considered that there is almost no interaction between the solid and the adsorptive molecule around a distance of adsorption with the fourth and fifth layers.

A theoretical density adsorption isotherm is created through integration of this density profile curve. Furthermore, theoretical density adsorption isotherms of various pore diameters are created from micropores to mesopores by changing the pore sizes.

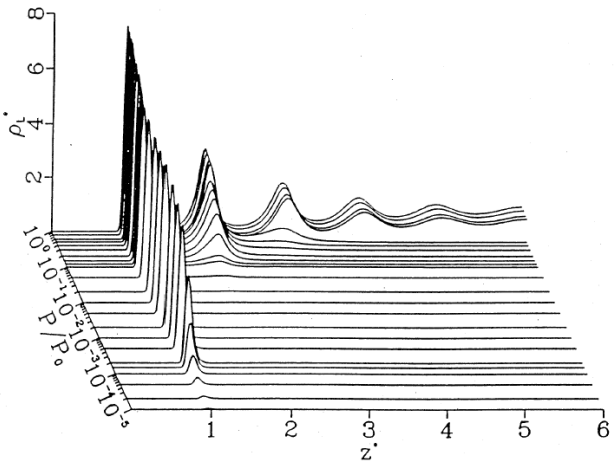


Fig. 1: Localized Density Profile using NLDFT
(P/P_0: Relative pressure, ρ_L*: Local density, Z*: Distance from carbon atom on graphite surface)

• Slit-shaped pore model

Pores with graphite structure, such as activated carbon and activated carbon fiber, are assumed to be slit shape.

An adsorption isotherm for slit-shaped pores is expressed with the equation below:

$$N(P)=\int_0^{\infty} dHf(H)\rho(P,H) \tag{29-16}$$

H: Pore width (nm)

Fluid interaction potential (ϕ_{ff}) can be calculated with the Lennard-Jones 12-6 potential.

$$\phi_{ff}(r)=4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12}-\left(\frac{\sigma_{ff}}{r}\right)^{6}\right] \tag{29-17}$$

Solid–fluid interaction potential (ϕ_{sf}) can be calculated with Steele 10-4-3 potential equation[3].

$$\phi_{sf}(z)=\varepsilon_w\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10}-\left(\frac{\sigma_{sf}}{z}\right)^{4}-\left(\frac{\sigma_{sf}^4}{3\Delta(z+0.61\Delta)^3}\right)\right] \tag{29-18}$$

$$\varepsilon_w=2\pi\varepsilon_{sf}\rho_s\sigma_{sf}^2\Delta \tag{29-19}$$

$$V_{ext}(z)=\phi_{sf}(z)+\phi_{sf}(H-z) \tag{29-20}$$

• Cylindrical pore model

Pores of regular mesoporous material (MCM41, FSM-16 and SBA-1), and zeolite with one-dimensional structure are assumed to be cylindrical shape.

An adsorption isotherm for cylindrical pores is expressed with the equation below:

$$N(P)=2\pi\int_{R_{\min}}^{R_{\max}} dRf(R)\rho(P,R)R \tag{29-21}$$

R: Pore radius (nm)

Fluid interaction potential (ϕ_{ff}) is calculated with Lennard-Jones 12-6 potential equation (29-17).
Solid–fluid interaction (ϕ_{sf}) for cylindrical pore model can be calculated with the equation below[10].

$$\phi_{sf}(r)=\varepsilon_{cw}\left[\frac{63}{32}\left(\frac{R-r}{\sigma_{sf}}\left(1+\frac{r}{R}\right)\right)^{-10}\times F\left(-\frac{9}{2},-\frac{9}{2};1;\left(\frac{r}{R}\right)^2\right)-3\left(\frac{R-r}{\sigma_{sf}}\left(1+\frac{r}{R}\right)\right)^{-4}\times F\left(-\frac{3}{2},-\frac{3}{2};1;\left(\frac{r}{R}\right)^2\right)\right] \quad (29\text{-}22)$$

$F(\alpha,\beta;\chi;\sigma)$ is a generalized geometrical function, and r is a radial coordinate relative to the center of pore.

$$\varepsilon_{cw}=\pi^2\varepsilon_{sf}\rho_s\sigma_{sf}^2 \quad (29\text{-}23)$$

$$V_{ext}(r)=\phi_{sf}(r)+\phi_{sf}(R-r) \quad (29\text{-}24)$$

• Calculation parameters

To create theoretical adsorption isotherms based on NLDFT, definition of individual parameters are essential. Actually, these parameters are not unified, which are different depending on each thesis. Intrinsically, parameters (Table 1) related to interaction of adsorptive (fluid) should be identical to those of the GCMC method described later.

The cause of the difference in the parameters between NLDFT and GCMC is considered to be the difference in assumptions that NLDFT and GCMC are based on, that is, DFT assumes that diatomic molecule is approximated to spherical shape.

To determine the parameters, it is recommended that you use the values that make the physical properties of the bulk calculated from the relevant parameters (saturation vapor pressure, surface tension, density, etc.) identical to the values given in documents.

The BEL software uses the following values:

Table 1. Parameters of the adsorptive-adsorptive intermolecular potential.[5]

Gas	ε_{ff}/k_b (K)	σ_{ff} (nm)	d_{HS} (nm)
Nitrogen	94.45	0.3575	0.3575
Argon	118.05	0.3305	0.3390
Carbon dioxide	253.9	0.3454	0.3495

ε_{ff}/k is approximated by a spherical Lennard-Jones interaction.

The solid adsorption interaction parameters are obtained by fitting to a multiple molecular layer adsorption isotherms for nonporous materials (Table 2).

Table 2. Parameters of adsorptive-adsorbent intermolecular potentials[7]

Gas-Solid	ε_{sf}/k_b (K)	σ_{sf} (nm)
Nitrogen/Carbon	53.22 (Cylinder) / 53.72 (Slit)	0.3494
Carbon dioxide/Carbon	81.5	0.3430
Nitrogen/Siliceous	147.3	0.3170
Argon/Siliceous	171.24	0.3000

ε_{sf}/k was obtained by fitting to adsorption data for a nonporous material having the same chemical structure as the porous material.

For the parameters related to the adsorbent (solid), this software uses the following values for slit-shaped pores and cylindrical pores (Table 3).

Table 3. Solid density of adsorbent[7]

Adsorbent	slit pore		Surface molecule number Ns (nm^{-2}) in cylinder and spherical pore
	Δ(nm) / layer spacing	ρ_s (nm^{-3})	
Carbon	0.335	114	38.19
Siliceous	-	-	15.3

3) Theoretical density adsorption isotherm (Kernel)

Fig. 2 and Fig. 3 show theoretical density adsorption isotherms actually calculated.

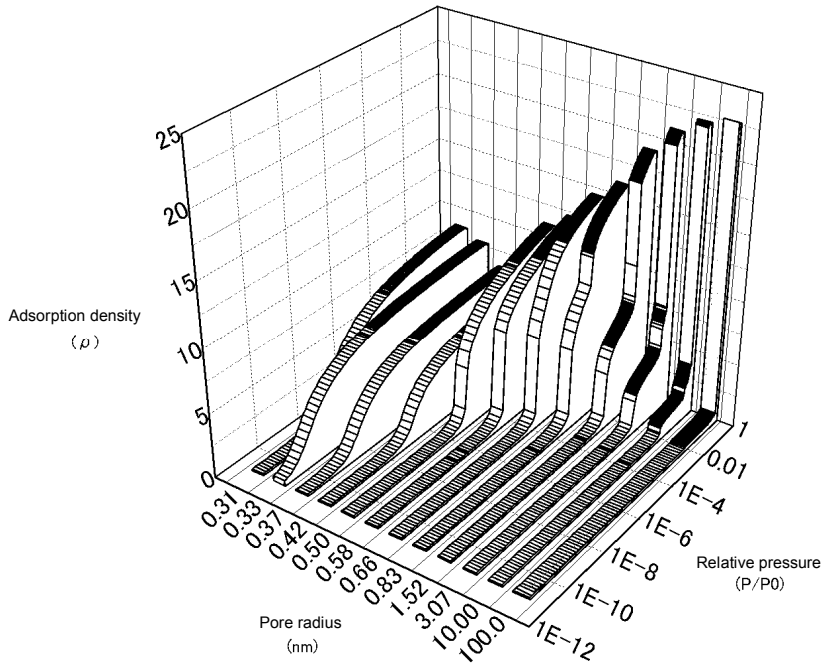


Fig. 2 Theoretical Density Adsorption Isotherm
(Parameters: Cylindrical pore, Adsorptive molecule: Ar, Pore surface atom: O)

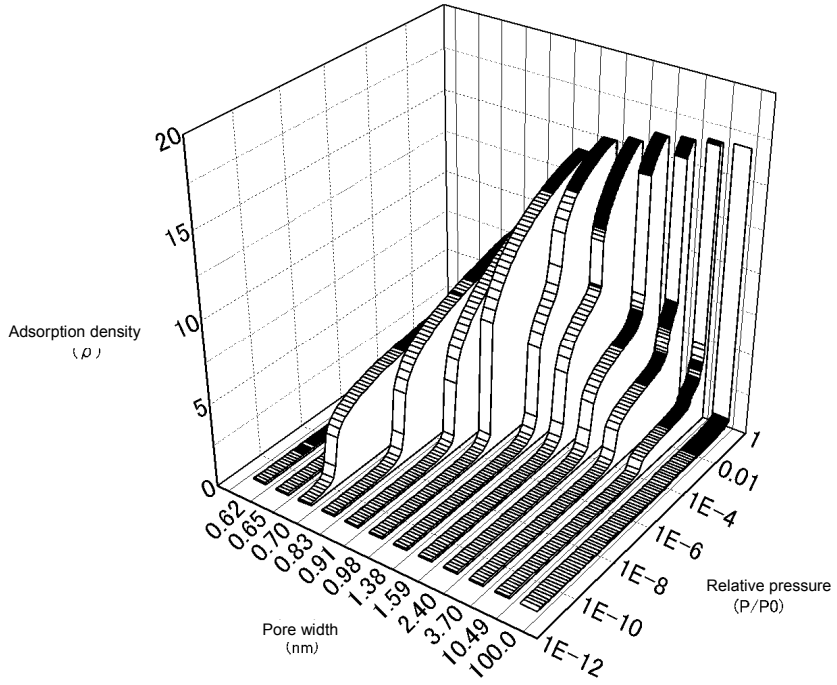


Fig. 3 Theoretical Density Adsorption Isotherm
(Parameters: Slit-shaped pore, Adsorptive molecule: N_2, Pore surface atom: C)

In Fig. 2 and Fig. 3, condensation pressure increases, as the pore diameter becomes large. These figure exactly reproduces that the Type I isotherm is shown in the micropore range, and it will change to Type IV in the mesopore range. An interesting point is that the pore condensation pressure is high at a point of the smallest pore diameter.

This means that the relevant molecule manage to enter the pore under high pressure condition, when the molecule size is close to the pore diameter. It is a feature of the NLDFT/GCMC method that such a condition can be reproduced, which is not available with other pore distribution analysis theories. Furthermore, the NLDFT/GCMC method can exactly reproduce occurrence of condensation in pores after a monomolecular adsorption layer is formed, if the pore diameter is several nanometers or larger.

4) GCMC

Adsorption simulation using the GCMC method executes the following steps repeatedly: definition of parameters (pore diameter and shape, adsorptive molecule, adsorbent surface atom, etc.); actually placing the adsorptive molecules in the virtual space of the pore; simulation of movement, generation and annihilation of the adsorptive molecules; and receiving more molecules when the system energy is negative (stable), and restoring them if the system energy is in the contrary condition.

Normally, these steps are repeated by one or two million cycles. After that, the system checks if the system energy is reduced and becomes stable (adsorption equilibrium state), and then simulates an amount of adsorption with a certain pore diameter at certain pressure. Continuously, the system increases the number of molecules placed in the pore to raise the system pressure, and calculates the amount of equilibrium adsorption at the next pressure value. Thus, the GCMC method executes an actual adsorption experiment on a computer, to create an adsorption isotherm.

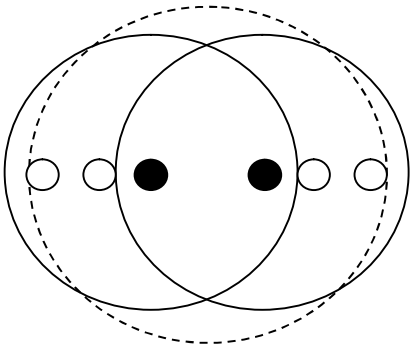


Fig. 4 Modeled N_2 molecule, -hard sphere system of DFT, -for GCMC (●: LJ center lx, ○: charge center lq)

In comparison between the GCMC and NLDFT methods, the NLDFT method assumes that adsorptive molecules are approximated to spherical shape, while the GCMC method assumes that N_2 and CO_2 molecules are placed at the LJ2/LJ3 center, to calculate interaction between actual molecules (atoms) by handling quadrupole moments (electric charges) individually (Fig. 4). With the NLDFT method, a point that minimizes energy is calculated. However, the GCMC method may not always provide accurate equilibrium state depending on preset conditions. Therefore, try-and-error (changing simulation sizes) is required for this method.

Table 4. Parameters of the adsorptive-adsorptive intermolecular potential[9)]

Gas	ε_{ff}/k_b (K)	σ_{ff} (nm)	lx (nm)	lq (nm)	q (e)
N_2	34.7 (Cylinder) / 101.5 (Slit)	0.334 (Cylinder) / 0.3615 (Slit9	±0.05047	±0.0847 ±0.1044	0.373 -0.373
Ar[10)]	118.05	0.3305	0	0	0
CO_2	C: 28.3 O: 81.0	C: 0.275 O: 0.3015	C: 0 O: ±0.1149	0 ±0.1149	0.6512 -0.3256
CH_4	148.75	0.37	0	0	0

Table 5. Parameters of adsorptive-adsorbent intermolecular potentials[9)]

Gas-Solid	ε_{sf}/k_b (K)	σ_{sf} (nm)	ε_{ss}/k_b (K)
N_2 / Carbon	25.0 (Cylinder) / 53.72 (Slit)	0.337 (Cylinder) / 0.3494 (Slit)	18 (Cylinder) / 28.43 (Slit)
CO_2 / Carbon	C: 25.0 O: 42.2	C: 0.308 O: 0.321	C: 22 O: 22
CH_4 / Carbon	57.2	0.355	22

5) Integral adsorption isotherm and pore distribution

In equations (1-16, 21), *N(P)* is an integral adsorption isotherm for slit-shaped pore model, and that for cylindrical pore model, respectively. $\rho(P, H)$ and $\rho(P, R)$ are theoretical adsorption isotherms for each pore diameter calculated by the NLDFT or GCMC method. To determine sample pore distribution, pore distribution functions (*f(H)*,*f(R)*) are changed for optimization by the least-squares method, so that IAE comes close to the measured adsorption isotherm.

$$N(P) = \int_0^{\infty} dH f(H) \rho(P, H)$$

$$N(P) = 2\pi \int_{R_{\min}}^{R_{\max}} dR f(R) \rho(P, R) R$$

Other pore distribution analysis theories use experimental data to execute pore distribution analysis, and therefore, the result will not change. However, with the method used by this system, the result may change depending on the fitting algorithm used by the computer software, because an integral adsorption isotherm based on the assumption of pore distribution is fit to experimental values. Therefore, it is necessary to verify whether the result is valid or not, by comparing IAE under analysis and experimental data, and by checking the analysis result with other information on the material. As described above, the theory for direct calculation from a conventional isotherm should be applied to a material whose information is unknown. On the other hand, for a material whose pore structure is well known and conforms to the assumption of the NLDFT/GCMC method, the NLDFT/GCMC method is preferable.

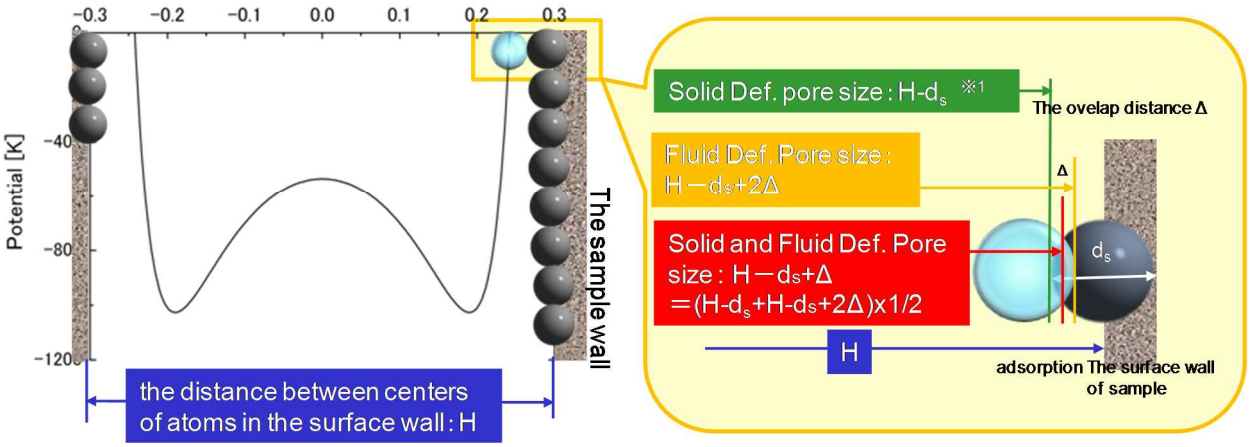
6) Definition of pore diameter

For definition of pore diameter, the following three methods are available:

[1] Solid Def. Pore Size: This definition adopts a definition developed by Gubbins et al., that is, “pore size determined by subtracting, from the distance between centers of atoms in the surface wall that forms the pore, the diametric value of surface atoms that are assumed to be solid spheres”. Our analysis software up to Ver. 6.1.0.9 adheres to this principle about pore size.

[2] Fluid Def. Pore Size: Kaneko et al. have reported that when the LJ potential occurring between the surface atom (which is assumed to be solid sphere) and adsorptive matter (which is assumed to be solid sphere) becomes zero, both atoms overlap with each other. “Distance across both ends of the adsorptive matter” in this situation is referred to as pore size.

[3] Solid and Fluid Def. Pore Size: Assuming that actual molecule is not a solid sphere, the pore size is defined as the “middle between pore size definitions (1) and (2)”. We recommend this pore size definition.

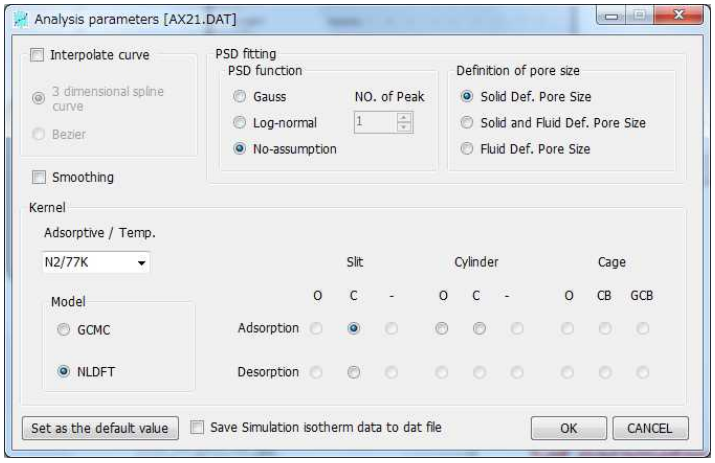


Reference

1) Tarazona, P., *Physical Review* **31**, 2672 (1985);
2) Tarazona, P., Marconi, U.M.B., Evans, R., *Mol Phys.* **52** 847 (1984).
3) Seaton, N.A., Walton, J.R.B., Quirke, N., *Carbon* **27,** 853 (1989).
4) Latoskie, C., Gubbins, K., Quirke, N., *J. Phys. Chem.* **97,** 4786 (1993).
5) Latoskie, C., Gubbins, K., Quirke, N., *Langmuir* **9**, 2693 (1993).
6) Olivier, J.P., *J. Porous Mat.* **2**, 9 (1995).
7) Ravikovitch, P., Vishnyakov, A., Neimark, A.V., *Physical review* **64**, 011602-1 (2001).
8) Neimark, A.V., *Langmuir* **11**, 4183 (1995).
9) Sweatman, M. B., Quirke, N., *J. Phys. Chem.*, **105**, 1403 (2001).
10) Ravikovitch, P.I., Vishnyakov, A., Russo,R., Neimark, A.V., *Langmuir* **16**, 2311 (2000).
11) “Nitrogen Adsorption in Slit Pores at Ambient Temperatures: Comparison of Simulation and Experiment”, K. Kaneko, *Langmuir,* **10**, 4606 (1994)
12) ”A STATISTICAL MECHANICS INTERPRETATION OF THE ADSORPTION ISOTHERM OFFOR THE CHARACTTERIZATION OF POROUS SORBENTS”, by Christian Matthew Lastoskie, May (1994)

29-2. Operation

1. If you select “NLDFT/DCMC method” from the “Analysis” menu and select a “.dat” file, the “Analysis parameters” window appears as shown below.



- **Interpolate curve**
  Executes interpolation (spline cubical or Bezier curve interpolation) of analysis data (pore distribution and ideal adsorption isotherm).

PSD fitting

- **PSD function (Distribution function)**
  Specify a distribution function that defines pore distribution.
- **No. of peaks**
  Estimate the number of peaks in pore distribution, and then specify the number. The number of peaks possibly entered is: 1 when the distribution function selected is “Gauss” and 1 to 5 when the distribution function selected is “log-normal”. (Allow the axis abscissa of the adsorption isothermal curve to represent Log scale; assume that the number of peaks at the rising phase in terms of amount adsorbed corresponds with the minimum number of peaks in pore distribution, and then enter a number greater than this number of peaks. Incidentally, for a particular material whose pores have been positively regulated, enter the number of peaks found with its pore distribution).
- **Smoothing**
  One point of around at all points pf PSD can be perfoemed moving average processing. It is a process that used only for PSD display.

- **Definition of pore size**
  Possible definitions of pore size (any definition can be selected from the following options (1) through (3) only if solid surface state “C” has been selected)
  (1) Solid Def. Pore Size: This definition adopts a definition developed by Gubbins et al., that is, “pore size determined by subtracting, from the distance between centers of atoms in the surface wall that forms the pore, the diametric value of surface atoms that are assumed to be solid spheres”. Our analysis software up to Ver. 6.1.0.9 adheres to this principle about pore size.
  (2) Fluid Def. Pore Size: Kaneko et al. have reported that when the LJ potential occurring between the surface atom (which is assumed to be solid sphere) and adsorptive matter (which is assumed to be solid sphere) becomes zero, both atoms overlap with each other. “Distance across both ends of the adsorptive matter” in this situation is referred to as pore size.
  (3) Solid and Fluid Def. Pore Size: Assuming that actual molecule is not a solid sphere, the pore size is defined as the “middle between pore size definitions (1) and (2)”. We recommend this pore size definition
- **Saving as the default value**
  If this item is checked, an ideal adsorption isotherm is saved in a file, which is named “Original file name + “_” + Sim”.

- **Model**
  Specify a set of particular model data (database) applied to various intended analysis operations. This database consists of information about adsorptive matters, adsorption temperatures, surface states of solids (O: oxygen, C; carbon, CB: Carbon Black, GCB: graphite carbon, and shapes of pores (slit or cylinder)). Choose a model database that appears to best represent the measuring conditions and sampling conditions for the set of intended measurement data; and then start analysis operation. Note that it is impossible to analyze a model whose database files have not yet been registered.

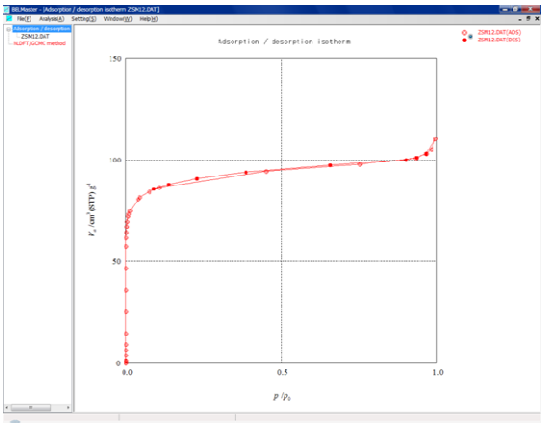
  We currently offer the kernel described later.

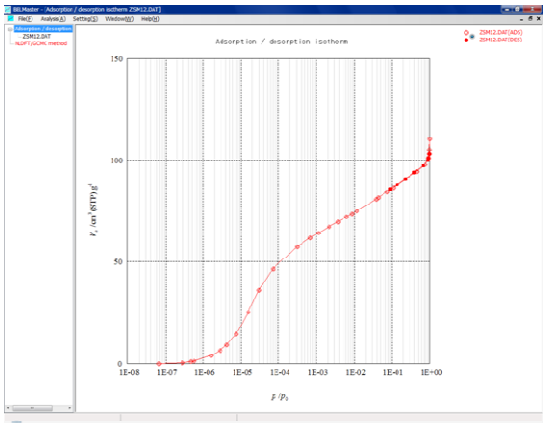
		Slit			Cylinder		
NLDFT	N_2 77 K	O	C	-	O	C	-
		-	O des.	-	O	O	
	Ar 87 K	O	CB	GCB	O	CB	GCB
		-	-	-	O	O	O
	CO_2 298 K	O	C	-	O	CB	GCB
		-	-	-	-	-	-
GCMC	N_2 77 K	O	C	-	O	C	-
		-	O des.	-	O	O	
	Ar 87 K	O	CB	GCB	O	CB	GCB
		-	-	-	O	-	-
	CO_2 298 K	O	C	UMPC*	O	CB	GCB
		-	O	O	-	O	O

  It is suitable for the analysis for 0.1 MPa (pore width 0.32 – 1.5 nm) or less

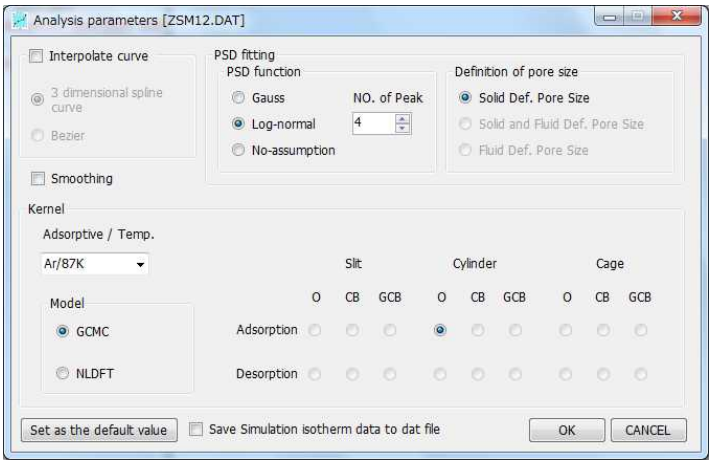
2. After specifying the analysis parameters, press the [OK] button to start calculation. After calculation is completed, a pore distribution curve and ideal adsorption isotherm data are displayed.

3. The procedure for executing analysis using the NLDFT/GCMC method is described below. The figure below shows an adsorption isotherm, which is obtained by actual measurement of Ar adsorption in zeolite (ZSM-12) that has micropores. First, set the X axis to the “log” scale in “X-axis display settings”. For the setting procedure, refer to page 37 of this manual.

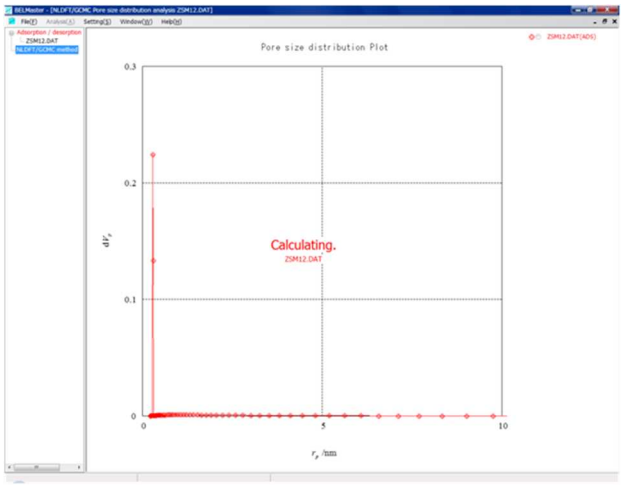




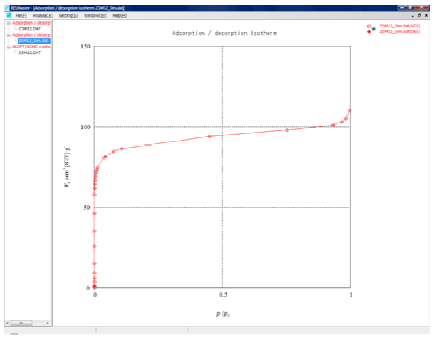
4. Specify the analysis parameters as shown on the right. These data are intended for GCMC analysis. Press the [OK] button to start calculation. (Analysis conditions: Distribution function: log-normal, Number of peaks: 4, Cylindrical, Oxygen, Ar/87 K)



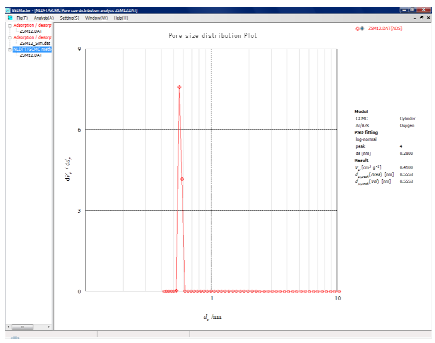
5. During calculation, the window as shown on the right is displayed.



6. After calculation is completed, ideal adsorption isotherm and pore distribution curve are displayed as shown below. The file name for the ideal adsorption isotherm is “ZSM-12_Sim.DAT”.

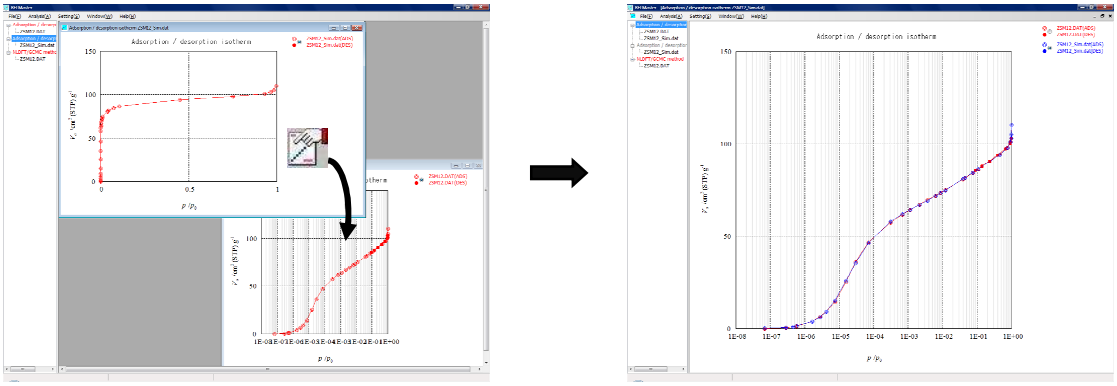


Ideal adsorption isotherm

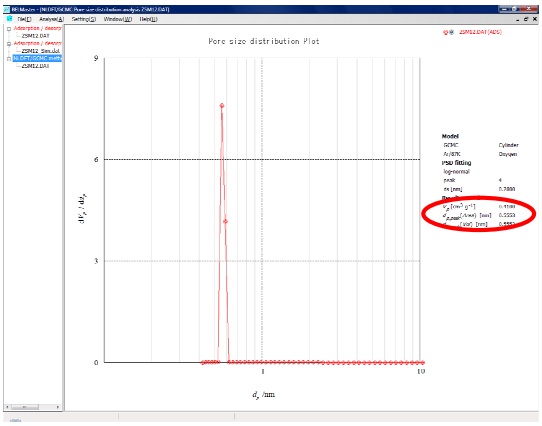


Pore distributiona curve

7. Place the actually measured adsorption isotherm on the ideal adsorption isotherm. You can see that the actually measured adsorption isotherm is well fitting to the ideal adsorption isotherm. If these isotherms are not well fit to each other, an accurate simulation result cannot be obtained.



8. The figure below shows a pore distribution curve for GCMC analysis. The pore diameter peak is 0.56 nm (based on GCMC analysis result). You can see that the distribution is well fitting to the ZSM12 structure (MTW: one-dimensional structure, dodecagon ring, 0.56 × 0.59 × 0.6).



GCMC analysis

As shown above, PSD acquisition from NLDFT/GCMC analysis enables you to obtain highly reliable data, if the assumed pore shape (cylindrical or slit) and chemical structure of the pore surface conform to those of the measured data.

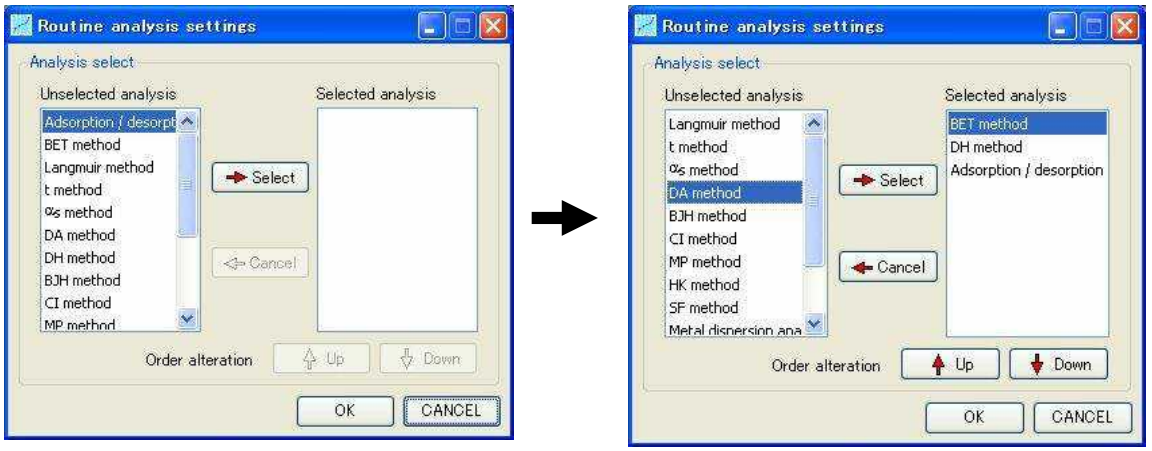
Chapter 30: How to use [Routine analysis]

Using this function, you can open selected data with multiple preset analysis methods.

30-1. Settings

1. Select “Routine analysis setting” on the “Setting” menu and a “Routine analysis settings” window will appear to allow you to change routine analysis settings.

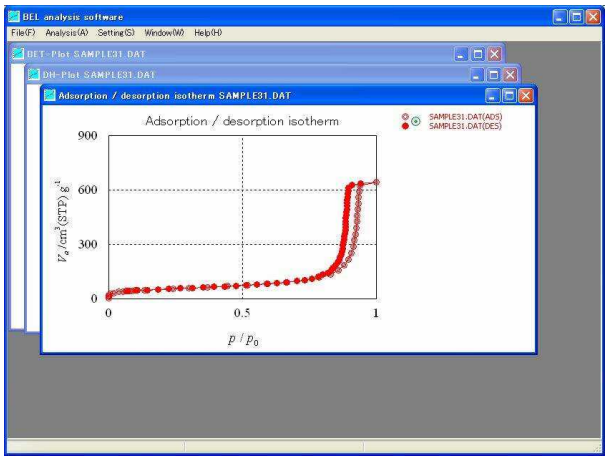
2. Select analyses you want to use from the “Unselected analysis” list. Then click on the [Select] button. The selected analysis names will be moved to the “Selected analysis” list. These are now added to the selected analyses.



30-2. Operation

1. Select “Routine Analysis” on the analysis menu. The file selection screen will appear.

2. As shown in the figure on the right, the analyses registered in “Routine analysis settings (R)” will open immediately.



Output an analysis report

Chapter 31: Output an analysis report

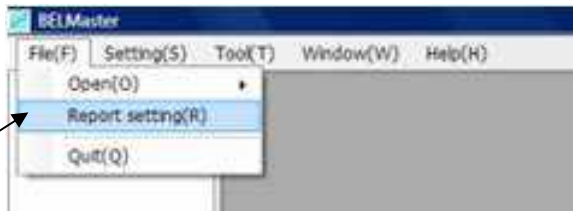
You can output numerical data or graphs as an Excel file (*.XLS), and can be edited with Excel. This function is useful to prepare reports. For equivalent weight differential heat of adsorption, difference adsorption isotherm, and molecular probe method, the analysis report output function is disabled.

Note) If Microsoft® Excel is not installed, this function cannot be used.

Settings Using this function, you can open selected data with multiple preset analysis methods.

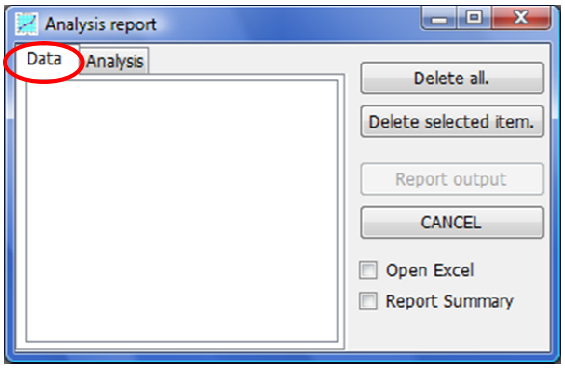
31-1. Operation

1. Select “Report settings” in the “File” menu.

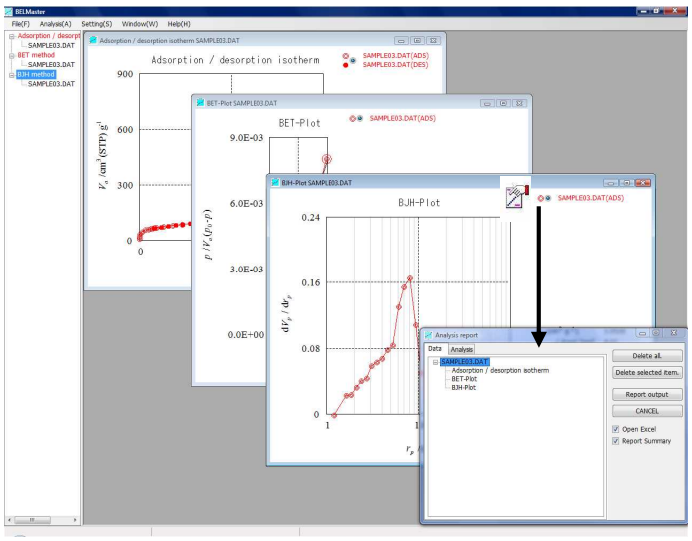


2. The “Analysis report” window appears as shown on the right.

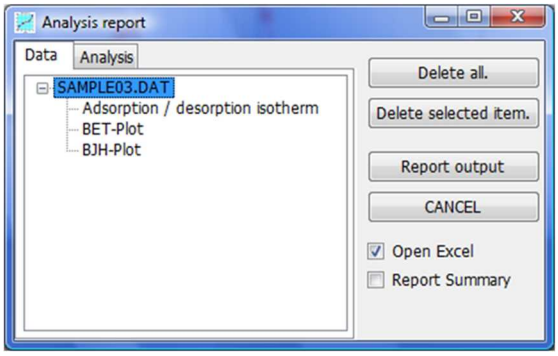
To output a report of several analysis results with the same data, select “data”.



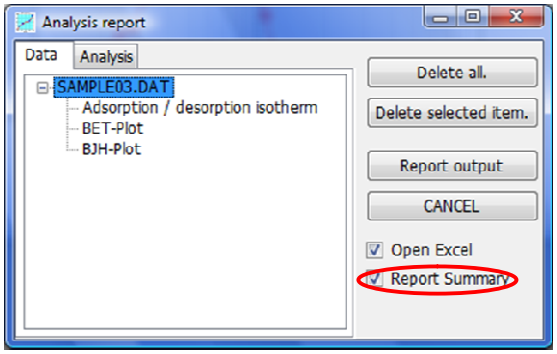
3. Drag and drop analysis data from a desired analysis window into the “Analysis report” window to copy the analysis data. The data at the time of copying will be output in an analysis report. After the data is copied, any setting change will not be reflected in the report.



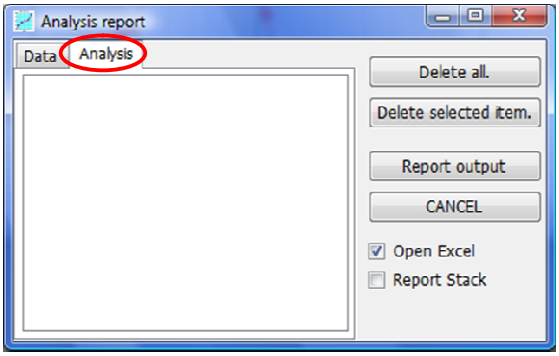
4. After the data is copied, the Analysis report settings window is displayed as shown on the right.



5. If the “Report Summary” checkbox is checked, a summary report will be prepared.

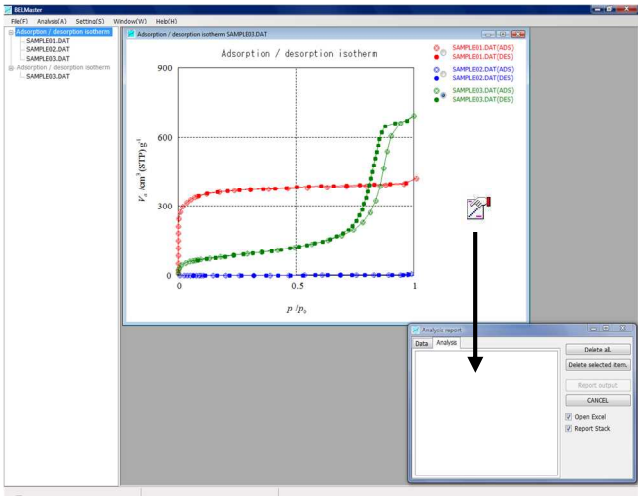


6. When two or more data are displayed in a single graph, or a report output of analysis results of the same analysis method from different files, select “Same analysis”.

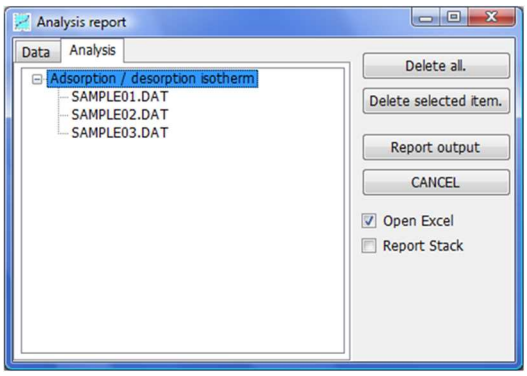


7. Drag and drop analysis data from a desired analysis window into the “Analysis report” window to copy the analysis data.

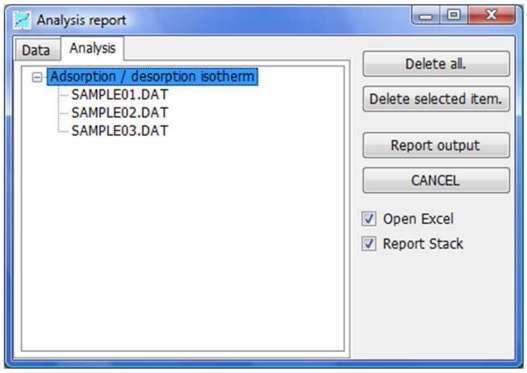
The data at the time of coping will be output in an analysis report. After the data is copied, any setting change will not be reflected in the report.



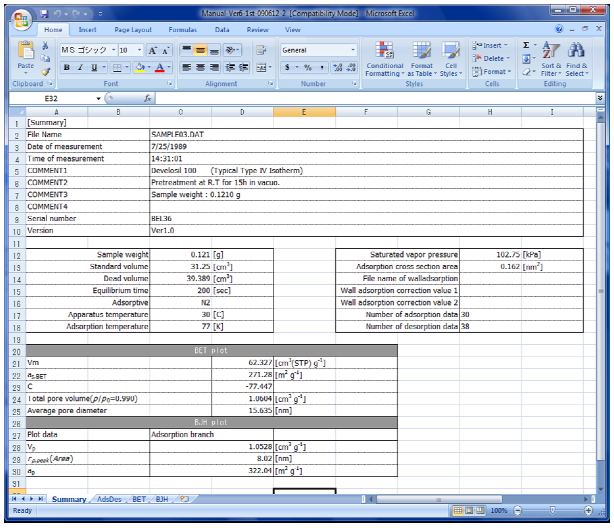
8. After the data is copied, the Analysis report window is displayed as shown on the right.



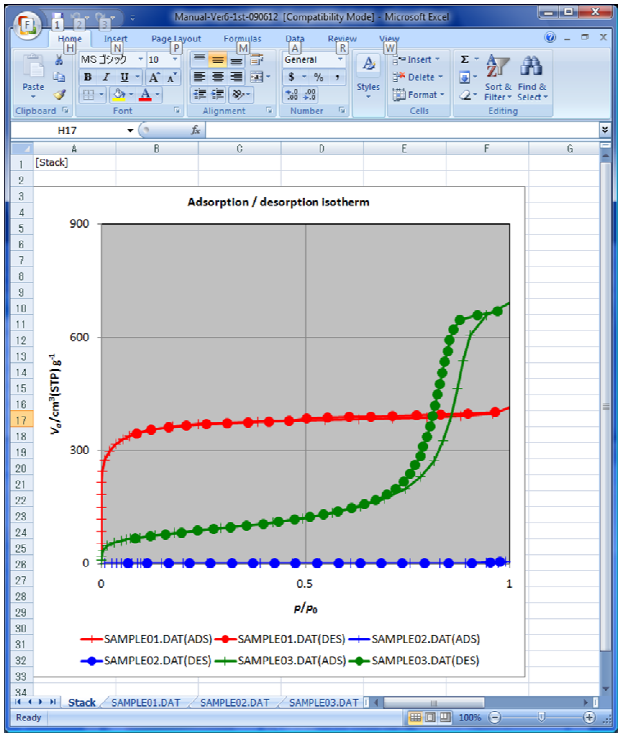
9. To output an overlap graph, mark an “Report stack” checkbox.



10. If you select a file to be output and press the [Report output] button, the file name setting window opens. If you specify a file name, an Excel worksheet will be prepared. In the worksheet, a graph is located below numerical data.

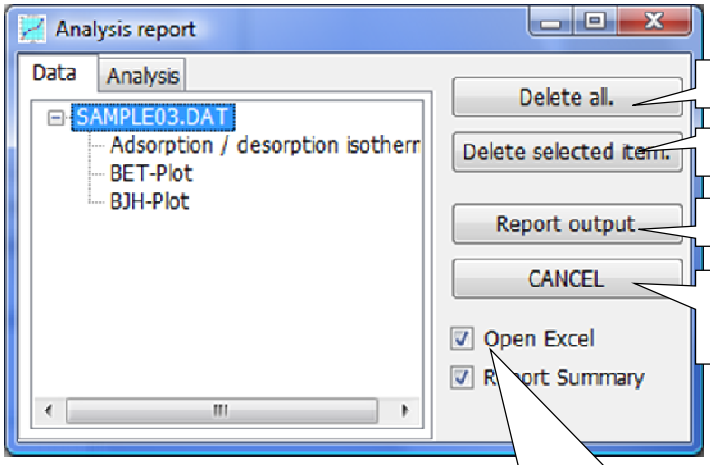


Report summary



Report stack

11. Other functions of the “Analysis” window are as follows:



Deletes copied data.

Deletes a selected item only.

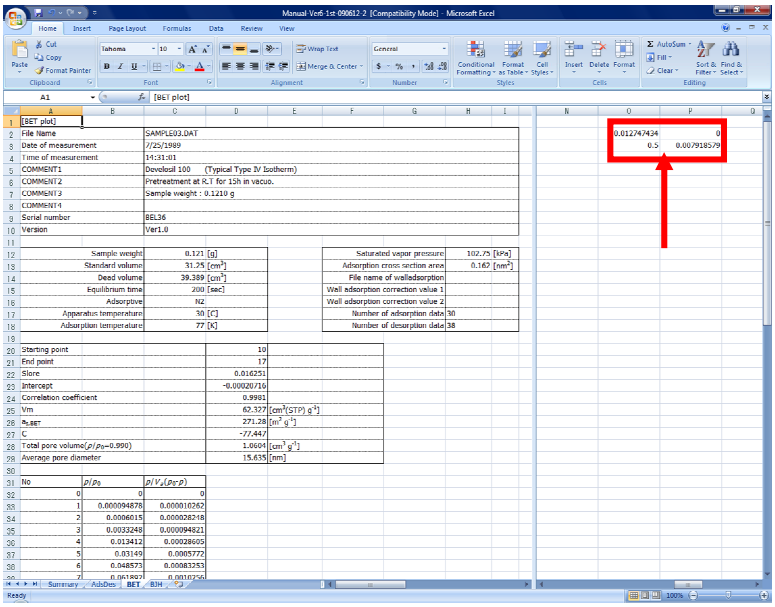
Outputs an analysis report.

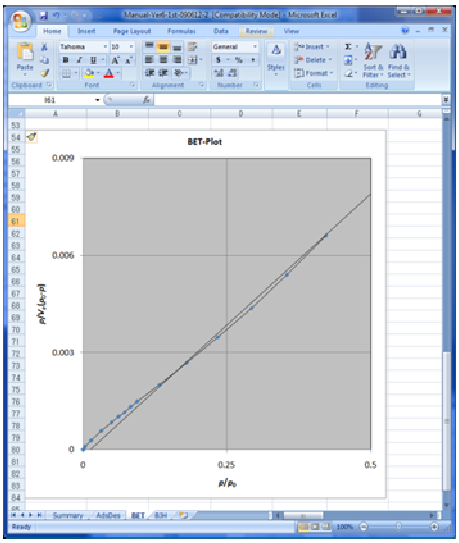
Closes the “Analysis report” window.

When this checkbox is ON, Excel will open after an analysis report is output.

—Output of report—

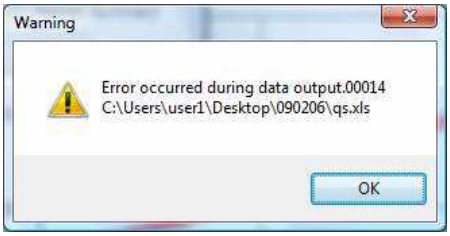
Using two points in least-squares method, the start point and end point of BET-plot, Langmuir plot, t plot, α_s plot, DA-plot, are displaid in these plot output report as shown below. Top step is the start point and bottom step is the end point.





31-2. Setting change

When you use “Analysis report” function, an error (00014) might be displayed as below.

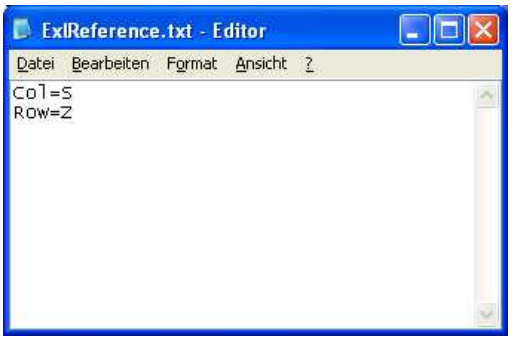


Refering to a cell within an Excel worksheet, a reference style where both the rows and the columns on the worksheet are numbered can be used. (In English version, the style is called “R1C1” reference style). This style is different in linguistic versions of Excel and the error 00014 is caused. In this case, change a setting as below.

1. Close the analysis software.

2. Open “ExlReference.txt” file with a text editor software like “NotePad”. The file is in the folder which “BELmaster” program is installed.

3. Edit the contents of the file as follow and save it. Following example shows the changing to German version setting.



4. Run the analysis software again.

APPENDIX

Chapter 32: Sample analysis examples

This chapter shows analysis examples of typical samples.

32-1. Silica with mesopores

1. The figure on the right shows Nitrogen adsorption isotherms for three types of silica with mesopores (macropores).

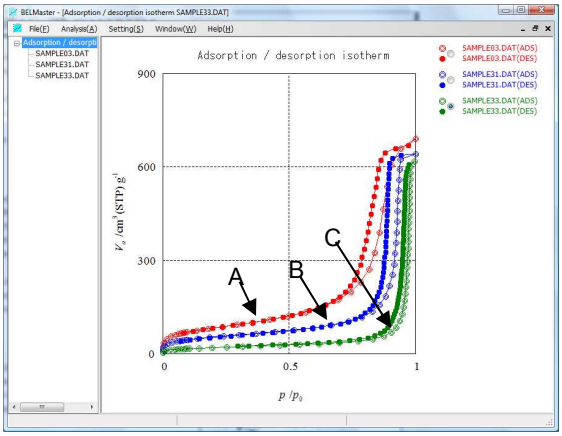
2. These adsorption isotherms display hysteresis (a part that does not match between adsorption process and desorption process), and are type IV adsorption isotherms.

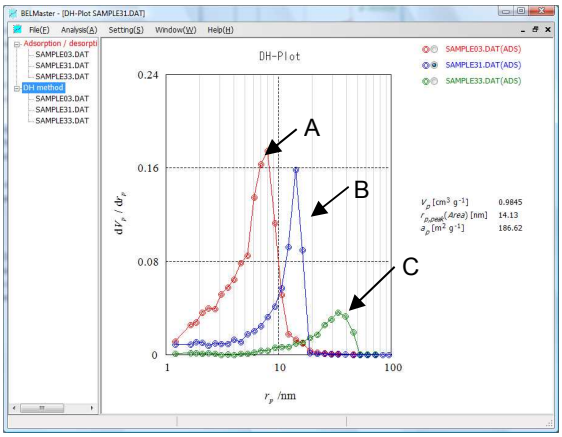
3. From these conditions, we can determine that these samples have mesopores.

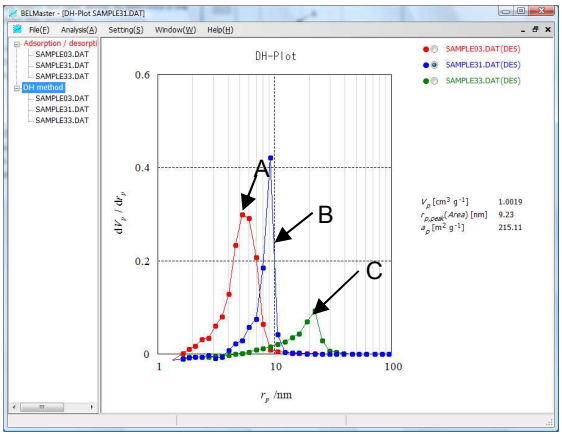
4. Since mesopore analysis theory is based on the Kelvin equation, the BJH plot, DH plot, and CI plot are suited for analysis. They are all based on the capillary tube condensation theory, and have almost no difference in the analysis results they provide.

5. The figure on the right is a result of the DH plot compared to the adsorption process. The distribution of pores can be obtained from the adsorption process.

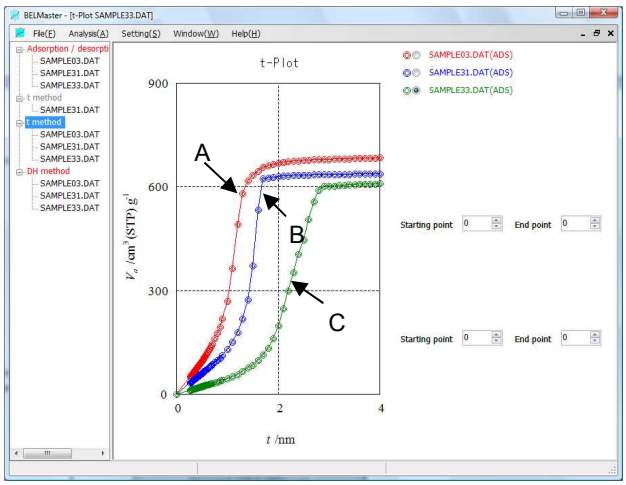
6. When the DH plot is used to the desorption process, the result is shown in the figure on the right, the pore distribution in the neck area (thinner part) can be obtained from the desorption process.







7. The figure on the right is the analysis result of a t -plot.

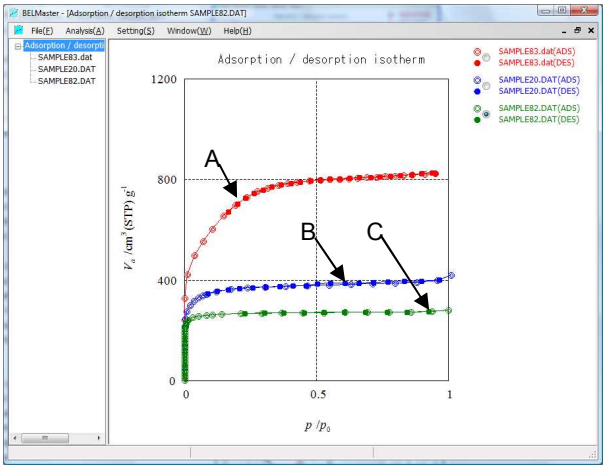


8. Data obtained using the BET plot, DH plot, and t plot are shown in the table below. We can evaluate sample information (specific area, pore volume etc.) from more than one analysis.

Sample	Silica A	Silica B	Silica C
BET plot	Specific surface / m^2g^{-1}		
	302	191	70.0
DH plot	[Adsorption process] Mesopore radius range / nm (Distribution peak value) / nm		
	2 to 15 (7.4)	5 to 18 (14)	up to 55 (37)
	[Adsorption process] Mesopore volume / cm^3g^{-1}		
	1.07	0.99	0.95
	[Desorption process] Mesopore radius range / nm (Distribution peak value) / nm		
	3 to 9 (5.7)	3 to 11 (8.8)	up to 35 (22)
	[Desorption process] Mesopore volume / cm^3g^{-1}		
	1.10	1.01	0.96
t plot	Specific surface / m^2g^{-1}		
	303	189	70.1
	External specific surface / m^2g^{-1}		
	6	4	9.8
	Mesopore specific surface / m^2g^{-1}		
	297	185	60.3
	Mesopore volume / cm^3g^{-1}		
	1.04	0.98	0.91

32-2. Activated carbon with micropores

1. The figure on the right shows Nitrogen adsorption isotherms for three types of activated carbon with micropores.

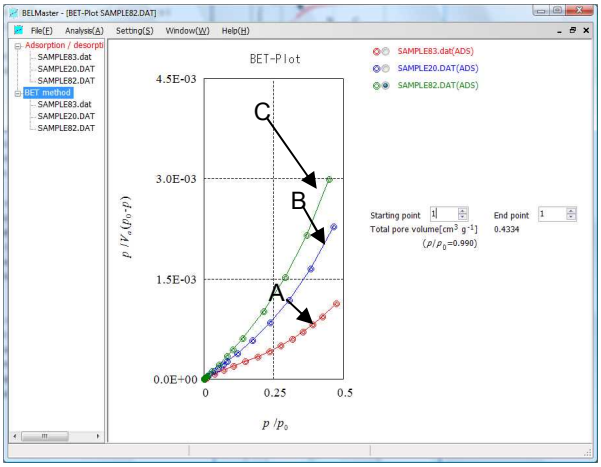


2. These adsorption isotherms have high adsorption volume at a relative low pressure range, and show a type I adsorption isotherm.

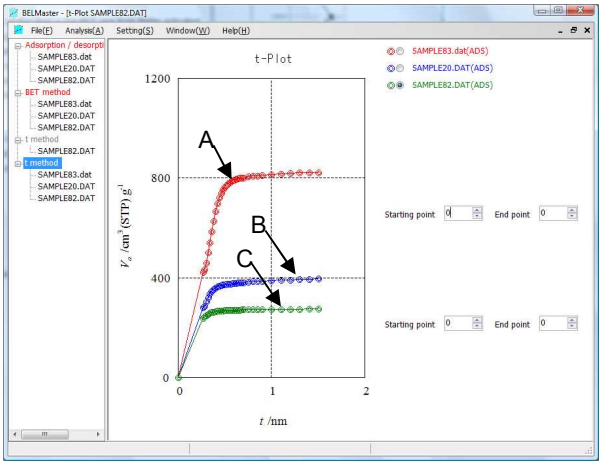
3. From these conditions, we can determine that these samples have micropores.

4. The BET plot calculates the specific area from the monomolecular layer adsorption volume, so evaluation of a specific area will be difficult if the sample pore width is less than 2x the molecular diameter of the adsorbate.

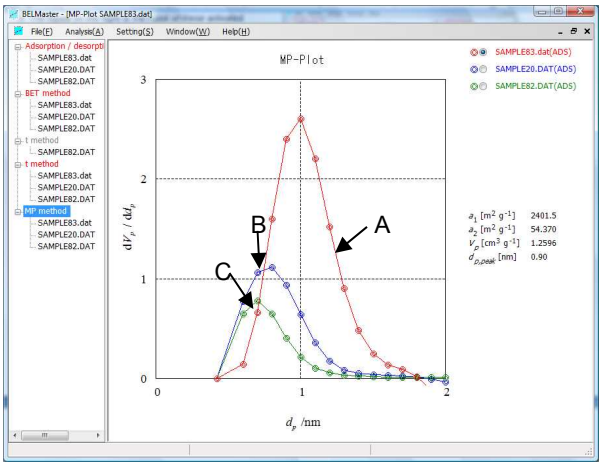
5. The figure on the right is the BET plot from these activated carbons. Activated carbon C has the smallest pore diameter, and the deviation from a straight line is large. Select the range for the straight line so that the C value will be a positive value at relatively low pressure. Then calculate the specific area.



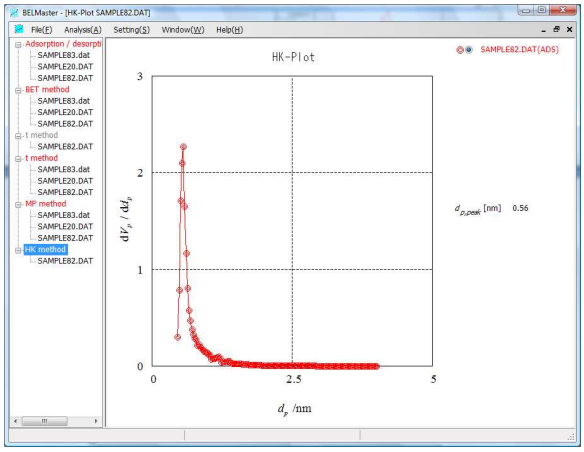
6. The figure on the right is the t-plot of these activated carbon samples. It is difficult to obtain the total specific area for activated carbon C. Also, as the pore diameter get smaller, the result may be greatly affected by the micropore effect and the total specific surface value will be larger than the actual value.



7. The analysis results from an MP plot are shown on the right.



8. The figure on the right is the HK plot of activated carbon C.



9. The table below sums up the data obtained using a BET plot, t plot, MP plot, and HK plot. From multiple analysis methods, we can evaluate sample information (such as the specific area and pore volume).

Sample	Activated carbon A	Activated carbon B	Activated carbon C
BET plot	Specific surface / m^2g^{-1}		
	2520	1410	(1070)
	C value (relative pressure range)		
	143 (0.01 to 0.2)	470 (0.02 to 0.08)	2900 (0.005 to 0.05)
t plot	Total specific surface / m^2g^{-1}		
	2550	1600	(1370)
	External specific surface/ m^2g^{-1}		
	100	60	20
	Micropore specific surface / m^2g^{-1}		
	2450	1540	(1350)
	Micropore volume / cm^3g^{-1}		
	1.17	0.55	0.41
	Pore width 2*t* / nm		
	0.95	0.71	-
MP plot	Micropore width range (Peak value of distribution) / nm		
	0.7 to 1.5 (0.9)	0.4 to 1.1 (0.80)	0.4 to 0.8 (0.60)
MP plot	Micropore width range (Peak value of distribution) / nm		
	-	-	0.4 to 0.7 (0.56)

Chapter 33: Major changes from version 5

- A sub window was added to the analysis screen.
- The analysis report function is available with Excel 2007.
- Summary report output is enabled with the analysis report function.
- PCT curve was added.
- For mesopore analysis, the INNES method was added.
- For the BJH, CI, DH and INNES methods, integrated pore volume and pore surface area in a specified range can be displayed.
- For the SF and HK methods, analysis point intervals were changed to "d_p: 0.025" and "r_p: 0.0125".
- For t-plotting, adsorption or desorption can be selected.
- The standard t curve of t-plot method was revised. (Graphitized carbon and non-graphitized carbon, silica, alumina, Document values, 2 items)
- "α_s" was added as the unit of Y-axis for adsorption isotherm.
- For BET analysis, the first point (0, 0) was added.
- For the BJH, CI, DH, MP, SF and HK methods, the units of the Y axis were unified to "dV_p/dr_p, $dV_p/d(\log r_p)$, dV_p/dd_p, $dV_p/d(\log d_p)$, ΣV_p".
- "*RH%*" was added as the unit of the X axis of adsorption isotherm.
- "*wt%*" was added as the unit of the Y axis of adsorption isotherm.
- Saturation vapor pressure can be changed in "Edite data" of the "Tool" menu.
- Up to ten graphs can be overlapped.
- BET analysis, Type I isotherm analysis (ISO9277) and 1-point analysis were added.
- For analysis of isosterioc heat of adsorption, analysis using three adsorption isotherms is enabled.
- "θ (Surface coverage)" was added as the unit of X-axis for analysis of isosterioc heat of adsorption.

Chapter 34: Standard isotherm

This chapter describes how to add a standard isotherm that is used for micropore analysis (t plot, α_s plot, and MP plot) to a mesopore analysis (DH plot, BHJ plot, and CI plot).

34-1. Standard isotherm

Micropore analyses (t-plot, α_s plot, and MP plot) and mesopore distribution analyses (DH plot, BJH plot, and CI plot) use a standard isotherm for their analyses. In nitrogen adsorption, this analysis program comes with data from 4 nonporous samples (silica, carbon (Graphitized Carbon and non-Graphitized Carbon), and alumina) , the standard t curves of Hrkins-Jula and FHH (Frenken-Halsey-Hill), and tow standard α_s curve for nonporous samples. Due to the difference of mutual effects between a sample surface and an adsorbate (nitrogen), there is a difference in the standard isotherm shown in figure 1. For this reason, we need to select a standard isotherm that is most like the surface characteristics of the sample. Especially, in the analysis of micropores, the standard isotherm selected greatly affects the results. Therefore, the "standard isotherm" is one of the most important parameters. In order to get better analysis data, a new standard isotherm can be added with some samples. A standard Hrkins-Jual t curve can be obtained using the equation below.

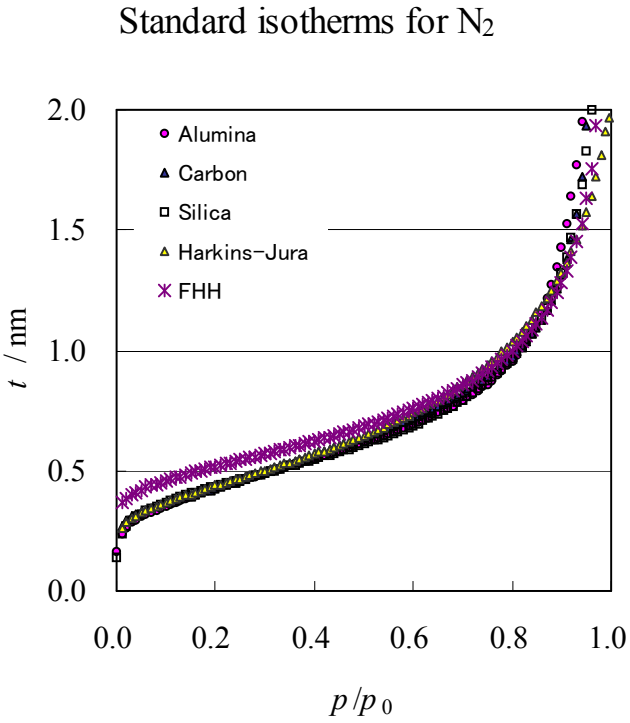


Figure1: Standard isotherm using BEL SORP analysis program

$$t = 0.1 \times \left[\frac{13.99}{0.034 - \log_{10}\left(\frac{p}{p_0}\right)} \right]^{\frac{1}{2}} \quad (1)$$

In addition, the standard FHH isotherm can be calculated using the equation below.

$$t = 0.354 \left[\frac{-5.00}{\ln\left(\frac{p}{p_0}\right)} \right]^{\frac{1}{3}} \quad (2)$$

The standard FHH t-curve matches well with an actually t-curve measured at a higher relative pressure range. However, it does not match in the medium and lower pressure ranges. Therefore, the analysis methods that use a standard t-curve in a relatively low pressure range, such as the t-plot and MP plot, may cause significant error and we cannot recommend use FHH for these methods.

1) Data configuration of a standard isotherm

The "standard isotherm" files are stored in the same directory where this software installed. The standard directory is "C: BEL JAPAN INC /T-DATA"

- Data configuration of a standard isotherm for t plot analysis

The standard isotherm file for a t plot has file name extension of ".t".

File name	Sample
"Silica-BET.t"	Silica
"NGCB-BEL.t"	non-Graphitized Carbon
"GCB-BEL.t"	Graphitized Carbon
"Alumina.t"	Alumina
"Harkins-Jula.t"	-
"FHH.t"	-

File format: Since the file is encrypted, it cannot be read with commercially-available spreadsheet software.

- Data configuration of a standard isotherm for αs plot analysis

Standard isotherm file for αs plot: Extension of file name is ".as ".

File name	Sample
"Silica-BET.as"	Silica
"NGCB-BEL.as"	non-Graphitized Carbon
"GCB-BEL.as"	Graphitized Carbon
"Alumina.as"	Alumina

File format: Since the file is encrypted, it cannot be read with commercially-available spreadsheet software.

2) How to create a standard isotherm

1. Preparation of standard isotherm data

Read the adsorption volume (V / cm^3(S.T.P.) g^{-1}) compared to the relative pressure from a nitrogen adsorption isotherm graph of a non-porous sample that is going to be added as a standard isotherm. For details about the relative pressure to be read, see the relative pressures of standard isotherms attached to this program.

2. Conversion of adsorption volume

Convert the adsorption volume obtained in step 1 above, into a unit for the standard isotherm being created.

- To create a standard isotherm for t plot, MP plot, and mesopore distribution analysis:

Convert adsorption volume (V / cm^3(S.T.P.) g^{-1}) to adsorption layer thickness (t / nm). Here, Vm is monomolecular layer adsorption volume, and 0.354 is the monomolecular layer thickness.

$$t = \frac{V_a}{V_m} \times 0.354$$

- When to create a standard isotherm for the αs plot:

Convert adsorption volume (V / cm^3(S.T.P.) g-1) to αs (use an adsorption volume of relative pressure P/P_0=0.4 as 1). Here, $V_{0.4}$ refers to the adsorption volume (V / cm^3(S.T.P.) g^{-1}) at relative pressure P/P_0=0.4.

$$\alpha_s = \frac{V_a}{V_{0.4}}$$

3. Create a standard isotherm

Using a text editing program (such as "Memo pad"), create a standard isotherm file. Create a file in a text format with items separated by commas. Refer to "1) Data configuration of the standard isotherm" on page 157.

4. Save the standard isotherm file

Save the "standard isotherm data" you created in the directory where this program is installed. For file name

extension, refer to the above 1). For standard isotherm data configuration, refer to the table below.

- Data configuration of a standard isotherm for t plot analysis

Record structure:

Record number	Record detail	Detail of item	Detail of "Carbon.t" file
1	Header 1	Comment	"Standard t-curve for Carbon"
2	Header 2	Sample name	"Carbon"
3	Header 3	Comment 1: Adsorbate, Adsorption temperature / K	"N2", 77.00,78.00
4	Data header	Number of data [N]	100
5	Data 1	1st data: Relative pressure [p/p_0(1)], adsorption layer thickness [t / nm(1)]	0.01, 0.2686
6	Data 2	2nd data: Relative pressure [p/p_0(2)], adsorption layer thickness [t / nm(2)]	0.02, 0.2933
: :	: :	: :	: :
N+3	Data N	N th data: Relative pressure [p/p_0(N)], adsorption layer thickness [t / nm(N)]	0.995, 16.999

- Data configuration of a standard isotherm for α_s plot analysis

Record configuration:

Record number	Record detail	Detail of item	Detail of "Sio2.as" file
1	Header 1	Sample name	"Silica"
2	Header 2	Comment 1: Adsorbate, Adsorption temperature / K	"N2", 77
3	Header 3	Comment 2: Adsorbate density, Number of molecules, Specific area of the standard sample, Adsorption volume at relative pressure 0.4 /cm^3(STP)g^{-1}	0.808,28.02,6.20,2.178
4	Data header	Number of data [N]	71
5	Data 1	1st data: Relative pressure [p/p_0(1)], Adsorption volume [α_s(1) / ($p/p_{0(0.4)}$ = 1)]	0.01,0.44
6	Data 2	2nd data: Relative pressure [p/p_0(2)], Adsorption volume [α_s(2)/ ($p/p_{0(0.4)}$ = 1)]	0.02,0.48
: :		: :	: :
N+4	Data N	N th data: Relative pressure [p/p_0(N)], Adsorption volume [α_s(n) / ($p/p_{0(0.4)}$ = 1)]	0.99,10.04

Chapter 35: Measurement data file

35-1. Measurement data

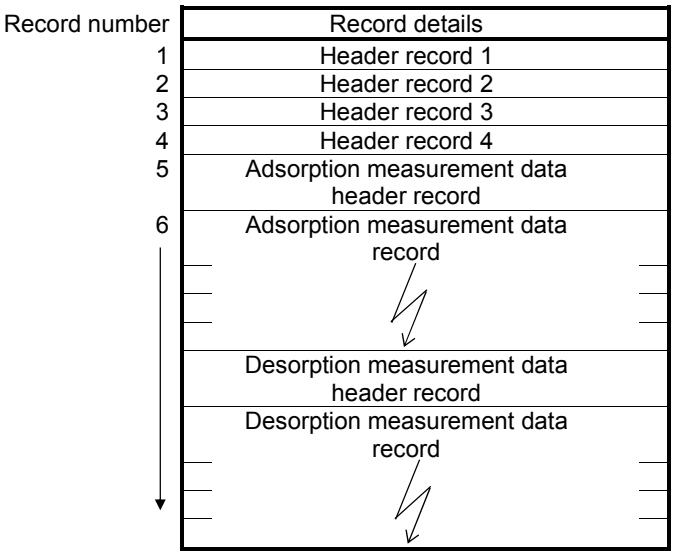
BEL SORP series “measurement data” are stored at each measurement step. During measurement, a “measurement data” file can be opened using this analysis program, and data can be analyzed, so that you can always see the measurement conditions.
In addition, the “measurement data” file is a text format file with items separated by commas. You can read the data using any commercial spreadsheet program.

Do not use any other program (except this analysis program) to open the “measurement data file” while making measurement. The measurement program won't be able to keep writing data.

The “measurement data” files are stored with file names that were specified during measurement. When you measure chemical adsorption using the BEL SORP 18, or BEL SORP 28SA, “-n th” will be added at the end of each file name. The file name extension is “.DAT”. The record configuration produced by each model is shown below.

35-2. BELSORP 28SA, BELSORP 18, and BELSORP HP series

Record structure:



Individual record details:

[Header record 1]

DATEMES	TIMEMES	COMMENT 1	COMMENT 2	COMMENT 3	COMMENT 4	DMY	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	DATEMEAS	Measurement start date	“YY/MM/DD”		○
2	TIMEMEAS	Measurement time	“HH:MM:SS”		○
3	Comment1	Comment 1st line	XXX～～～X	○	
4	Comment2	Comment 2nd line	XXX～～～X	○	
5	Comment3	Comment 3rd line	XXX～～～X	○	
6	Comment4	Comment 4th line	XXX～～～X	○	
7	DMY	“0.000000”	-	-	-

[Header record 2]

SERIAL_NO	VERSION	DMY	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	SIRIAL_NO	Measurement device Serial No.	XXX～～～X	-	-
2	VERSION	BEL-WINDOWS Version No.	XXX～～～X	-	-
3	DMY	“0.000000”	-	-	-

[Header record 3]

SW	Vs	Vd	EQT	ADS	TEMP1	TEMP2	P0	CS	ANLS1	ANLS2	ANLS3	ANLS4	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	SW	Sample weight (g)	9.99999	○	
2	Vs	Device main housing standard volume (cc)	ZZ9.99999	○	
3	Vd	Sample dead volume (cc)	ZZ9.99999		○
4	EQT	Equilibrium time (Pa/min)	ZZ9.99999	○	
5	ADS	Adsorbate name	XXX～～～X	○	
6	TEMP1	Thermostatic chamber temperature (˚C)	ZZ9.9	○	
7	TEMP2	Adsorption temperature (K)	ZZ9.9	○	
8	P0	Saturated vapor pressure (Torr)	ZZZ9.999999	○	○
9	CS	Adsorption cross section area (nm^2)	Z9.999	○	
10	ANLS1	“Sample molecular volume” (Written by the analysis program)	ZZ9.999	-	-
11	ANLS2	“Adsorbate molecular volume” (Written by the analysis program)	ZZ9.999	-	-
12	ANLS3	“Sample specific surface” (Written by the analysis program)	9.999E±Z9	-	-
13	ANLS4	Sample density (g cm^{-3}) (Written by the analysis program)	Z9.999	-	-

- Vs is one of 4 types, depending on the measurement conditions.
- “Saving sample density” is a function recently added to version 5.00 of the analysis program. Please note that if a file is opened (operations such as “edit data,” “save in a file” etc.) using version 5.00 of the analysis program, the file will not be readable by previous versions of the analysis program.

[Header record 4]

REFILE	REDATA_N	REDATA_K	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	REFILE	Wall surface adsorption correction file name	XXX～～～X	○	
2	REDATA_N	N value for wall surface adsorption correction	9.999E±Z9	○	
3	REDATA_K	K value for wall surface adsorption correction	9.999E±Z9	○	

[Adsorption measurement data header record]

K	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	K	Number of adsorption measurement points.	ZZ9		○

[Adsorption measurement data record]

PI(n)	PE(n)	PE2(n)	P0(n)	V(n)	CrLf

- There are the same number of records as the number of adsorption measurement points.
- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	PI(n)	Introducing pressure (Torr)	ZZZ9.99999		○
2	PE(n)	Open adsorption balance pressure V11 (Torr)	ZZZ9.99999		○
3	PE2(n)	Open adsorption balance pressure V11 (Torr)	ZZZ9.99999		○
4	P0(n)	Saturation vapor pressure (Torr)	ZZZ9.99999	○	○
5	V(n)	Total adsorption volume (ml[S.T.P]/g)	ZZZ9.99999		Calculated value

[Desorption measurement data header record

L	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	L	Number of desorption measurement points.	ZZ9		○

[Desorption measurement data record]

PI(n)	PE(n)	PE2(n)	P0(n)	V(n)	CrLf

- There are the same number of records as the number of desorption measurement points.
- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	PI(n)	Introducing pressure (Torr)	ZZZ9.99999		○
2	PE(n)	Open desorption balance pressure V11 (Torr)	ZZZ9.99999		○
3	PE2(n)	Open desorption balance pressure V11 (Torr)	ZZZ9.99999		○
4	P0(n)	Saturation vapor pressure (Torr)	ZZZ9.99999	○	○
5	V(n)	Total desorption volume (ml[S.T.P]/g)	ZZZ9.99999		Calculated value

Detail of the sample file:

See the attached document 1: “Sample of measurement data file (BE SORP 18, 28 series)”

35-3. BELSORP-mini, BELSORP-max, and BELSORP-aqua3 series

Record structure:

Record number	Record details	
1	Device information	Title
2		
3		
4		Device serial number
5		Standard volume/ml
6	Measurement conditions	Title
7		
8		
9		Adsorbate name
10		Adsorption temperature/K
11		Adsorption cross section area/nm^2
12		Adsorption molecular weight
13		Equilibrium time/sec
14		Measurement mode
15	Sample information	Title
16		
17		
18		Specimen weight/g
19		Comment 1
20		Comment 2
21		Comment 3
22		Comment 4
23		Specimen specific surface/$m^2 g^{-1}$
24		Specimen molecular weight
25		Specimen density/g cm^{-3}
26	Time, dead volume, etc.	Title
27		
28		
29		Measurement start date
30		Measurement time
31		Dead volume inclination
32		Dead volume slice
33		Initial dead volume /ml
34	Adsorption data	Title
35		
36		
37		
38		Adsorption measurement data record
↓		↓
	Desorption data	Title
		Desorption measurement data record
		↓

Each record detail:

[Device information]

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	===～～～=		
2			Device information		
3			===～～～=		
4	SIRIAL_NO	Device serial number	XXX～～～X	○	
5	VS_0	Standard volume/ml	9.999	○	

[Measurement conditions]

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	===～～～=		
2			Measurement conditions		
3			===～～～=		
4	Adsorbate name	Adsorbate name	XXX～～～X	○	
5	Adsorption temperature	Adsorption temperature/K	ZZ9.99	○	
6	Adsorption cross section area	Adsorption cross section area/nm^2	9.999	○	
7	-	Adsorption molecular weight	0.00 fixed	○	
8	Adsorption equilibrium time	Equilibrium time/sec	ZZZ9	○	
9	Number of measured specimen	Measurement mode	9	○	

[Sample information]

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	===～～～=		
2			Sample information		
3			===～～～=		
4	Sample weight	Specimen weight/g	9.9999	○	
5	Comment(1)	Comment1	XXX～～～X	○	
6	Comment(2)	Comment2	XXX～～～X	○	
7	Comment(3)	Comment3	XXX～～～X	○	
8	Comment(4)	Comment4	XXX～～～X	○	
9	-	Specimen specific surface/$m^2\ g^{-1}$	0.0000 fixed	○	
10	-	Specimen molecular weight	0.00 fixed	○	
11		Specimen density/g cm^{-3}	0.00 fixed		

[Time and dead volume]

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	===～～～=		
2			Time and dead volume		
3			===～～～=		
4	Measurement start date	Measurement start date	yy/mm/dd	○	
5	Measurement time	Measurement time	hh:nn:ss		○
6	Vd_a	Inclination of dead volume	9.9999E+9		○
7	Vd_b	Slice of dead volume	9.9999E+9		○
8	Ads_Vd	Initial dead volume/ml	Z9.999		○

[Adsorption data]

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	===～～～=		
2			Adsorption data		
3			===～～～=		
4			*1		
5	-	Adsorption measurement data record	-		○

*1 “No.” “Pe/kPa” “P0/kPa” “Vd/ml” “V/ml(STP) g^{-1}”

[Adsorption measurement data record]

- Adsorption data continues until the last record is 0.
- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	I	Adsorption point No.	ZZ9		○
2	PeT	Adsorption balance pressure *pe*/kPa	ZZ9.999		○
3	Ads_P0	Saturated vapor pressurep_0/kPa	ZZ9.999		○
4	Ads_Vd	Varied dead volume *Vd*/ml	ZZ9.999		○
5	Ads_V	Adsorption volume *V*/ml(STP)･g^{-1}	ZZ9.999		○

[Desorption data]

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	===～～～=		
2			Desorption data		
3			===～～～=		
4			*1		
5	-	Desorption measurement data record	-		○

*1 “No.” “Pe/kPa” “P0/kPa” “Vd/ml” “V/ml(STP) g^{-1}”

[Desorption measurement data record]

- Desorption data continues until the last record is 0.
- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	I	Desorption point No.	ZZ9		○
2	PeT	Desorption balance pressure *pe*/kPa	ZZ9.999		○
3	Des_P0	Saturated vapor pressurep_0/kPa	ZZ9.999		○
4	Des_Vd	Varied dead volume *Vd*/ml	ZZ9.999		○
5	Des_V	Desorption volume *V*/ml(STP)･g^{-1}	ZZ9.999		○

Detail of sample file:

See attached document 2: “Sample of a measurement data file (BELSORP - mini series)”

Attached document 1: “Sample of a measurement data file (BELSOPR18, 28 series)”

Record number

```
1   “00/04/22”,”18:56:34”,”M11-02”,””,””,””,0
2   “8080”,”「BELSORP 28 SA」”,.95
3   .1845,33.07,39.6463857184048,300,”N2”,40,77,2587.60289848465,.162,0,0,0,0
4   “”,0,0
5   57
6   30.22499,0.13655,0.16704,756.68931,6.15605
7   10.28261,0.20439,0.24255,756.51823,8.21997
8   10.35934,0.32888,0.37448,756.80775,10.26193
9   10.52676,0.64678,0.69666,756.62614,12.22716
10  10.84904,1.67837,1.71592,756.73668,13.87114
11  11.81831,4.06460,4.08934,756.66299,14.88598
12  14.26987,7.45042,7.47406,755.77563,15.45714
13  17.66201,11.15716,11.18962,755.94709,15.88117
14  21.34052,15.09593,15.12642,756.05763,16.19107
15  25.31851,19.21405,19.25691,756.01026,16.42748
16  29.47220,23.45081,23.50152,756.03131,16.61446
17  33.65731,27.71785,27.77536,755.56131,16.77515
18  38.00204,32.03359,32.10471,755.63125,16.92815
19  42.26915,36.36144,36.43583,755.86813,17.06268
20  46.67603,40.70449,40.79249,755.77563,17.20579
                    ⋮
73  48
74  861.80426,750.38212,752.03030,757.29842,185.46872
75  638.56709,741.92819,743.53276,757.08410,165.95147
76  662.16834,736.31258,737.90989,757.26834,151.75361
77  662.21107,730.20865,731.75917,757.08410,138.94215
78  658.07261,724.28785,725.87499,757.23074,126.46182
79  650.24738,717.29885,718.88163,757.53154,114.06537
80  643.81385,710.46246,712.00687,758.04741,101.71506
81  629.81668,699.01760,700.53150,757.32098,89.98415
82  624.44610,683.60519,685.07637,757.00515,81.30382
83  625.33320,670.08500,671.51345,756.91039,75.12944
84  618.04308,657.17520,658.60467,756.89987,69.96938
85  595.51961,640.11473,641.51877,756.75247,64.70894
86  592.39236,625.00752,626.35924,756.53139,61.43650
87  583.92826,611.54837,612.92189,756.59907,58.79593
88  573.27691,598.63857,599.93580,756.75247,56.48001
                    ⋮
```

Attached document 2: “Sample of a measurement data file (BELSOPR-mini series)”

Record number

```
1   ====================
2   Device information
3   ====================
4   “Device serial number:”          4Port
5   “Standard volume/ml:”            9.017
6   ====================
7   Measurement conditions
8   ====================
9   “Adsorbate name:”    N2
10  “Adsorption temperature/K:”      77.00
11  “Adsorption cross section area/nm2:”      0.162
12  “Adsorption molecular weight:”   0.00
13  “Equilibrium time/sec:”          300
14  “Measurement mode:”              2
15  ====================
16  Sample information
17  ====================
18  “Specimen weight/g:”             0.3039
19  “Comment 1:”         “CB”
20  “Comment 2:”         ““
21  “Comment 3:”         ““
22  “Comment 4:”         ““
23  “Specimen specific surface/m2･g-1:”       0.0000
24  “Specimen molecular weight:”     0.00
25  “Specimen density:”  0.00
26  ====================
27  Time and dead volume
28  ====================
29  “Measurement start date:”        2004/04/12
30  “Measurement time:”              24:25:09
31  “ Dead volume inclination:”      -1.547E-06   32
32  “ Dead volume slice:”            1.387E+01
33  “ Initial dead volume/ml:”       13.748
34  ====================
35  Adsorption data
36  ====================
37  “No.”     “Pe/kPa”   “P0/kPa”   “Vd/ml”    “V/ml(STP) g-1”
38  1         0.011811   103.47     13.723     4.4456
39  2         0.039506   103.4      13.691     9.3174
40  3         0.30627    103.35     13.668     13.92
41  4         2.6323     103.29     13.653     16.056
42  5         4.8454     103.24     13.639     16.629
                         ⋮
                         ⋮
87  50        103.29     103.44     13.299     543.96
88  0         0          0          0          0
89  ====================
90  Desorption data
91  ====================
92  “No.”     “Pe/kPa”   “P0/kPa”   “Vd/ml”    “V/ml(STP) g-1”
93  1         100.53     103.34     13.281     518.6
94  2         100.17     103.38     13.269     494.5
95  3         99.939     103.41     13.254     467.91
96  4         99.757     103.47     13.239     441.73
97  5         99.593     103.47     13.225     416.01
                         ⋮
                         ⋮
126 34        29.968     103.12     12.547     24.388
127 0         0          0          0          0
```

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