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>

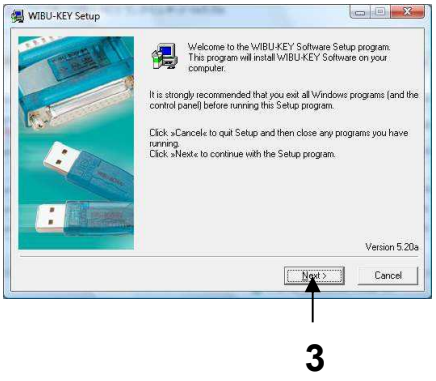
Chapter 2: Installation of the analysis program

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.)

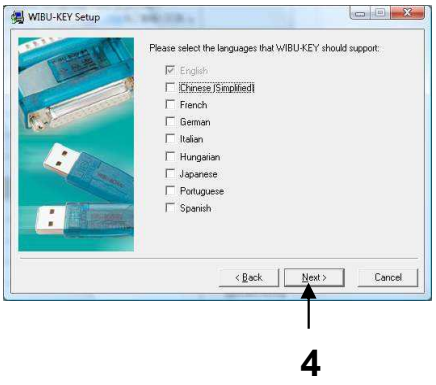
2-1. Installation of the WIBU-KEY program

* 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.)

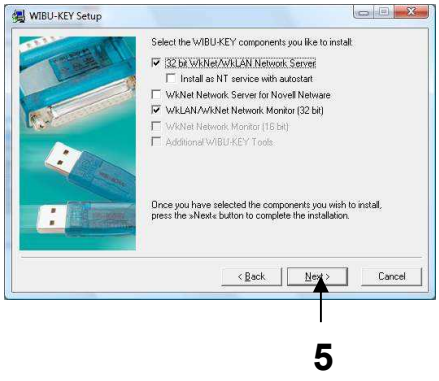
1. Put the Setup CD in the CD-ROM drive.
2. Run WkRt-Int.exe, which can be found in the WIBU-KEY device driver folder on the Setup CD. After reading this program for a moment, your PC displays the screen shown at right.
3. Click the [Next] button.



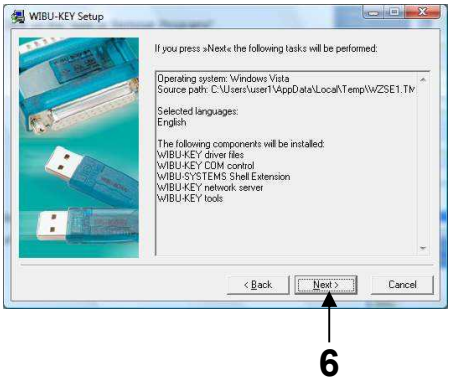
4. Choose “English” and then click the [Next] button.



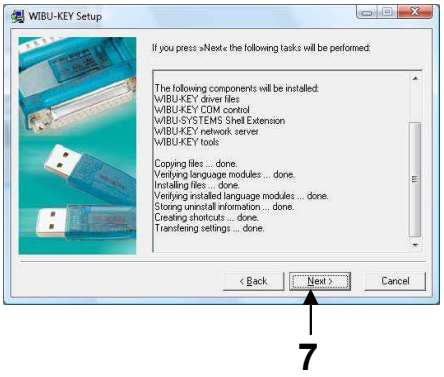
5. Click the [Next] button again.



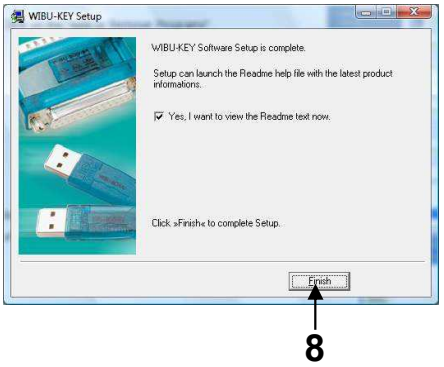
6. After clicking the [Next] button, your PC will start installing the WIBU-KEY driver.



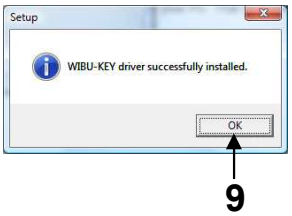
7. Click the [Next] button again.



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.)

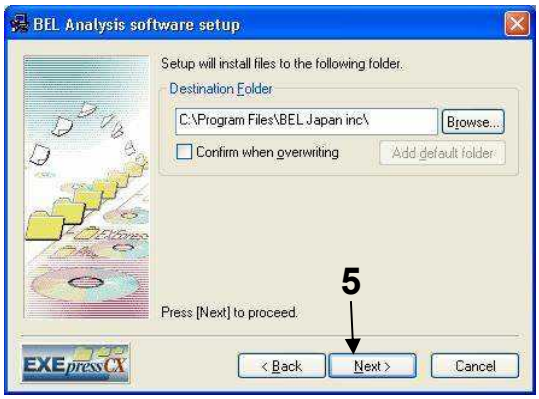
1. Put the Setup CD in the CD-ROM drive.

2. Run SETUP.EXE, which can be found in the Data analysis program folder on the Setup CD.

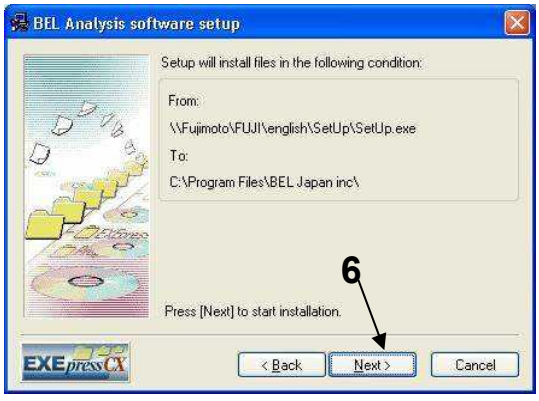
3. The installer will start and you will see window on the right.

4. Click the [Next] button.

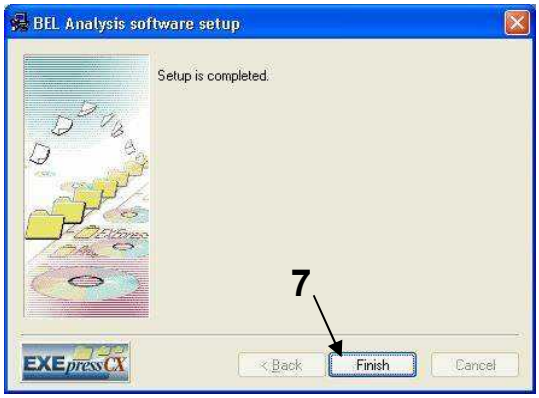
5. Confirm the installation destination folder and then click the [Next] button.



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.

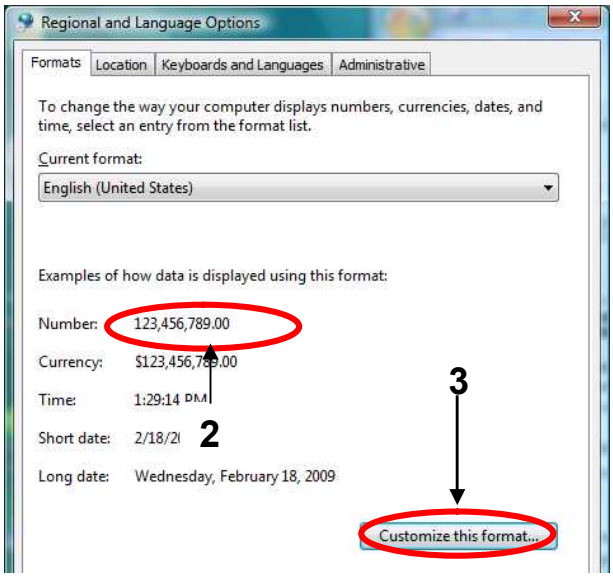
Folder configuration	Description	Details
BelAnalys	Installation folder	A different folder name can be used.
— BELMaster.exe	Execution file	
— *.dll	Expansion file used by the execution file	Be sure to place this file in the same folder as the execution file. Note: If you delete the expansion file, this 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.

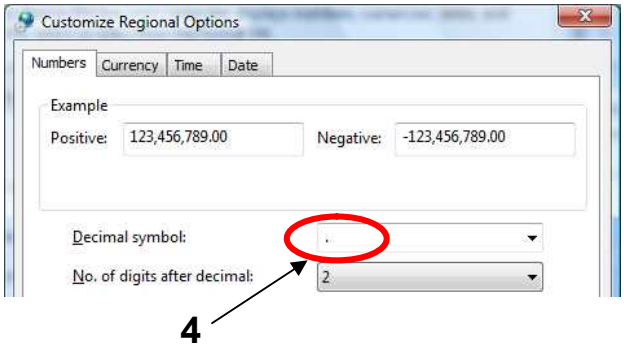
Specifying a decimal point

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.

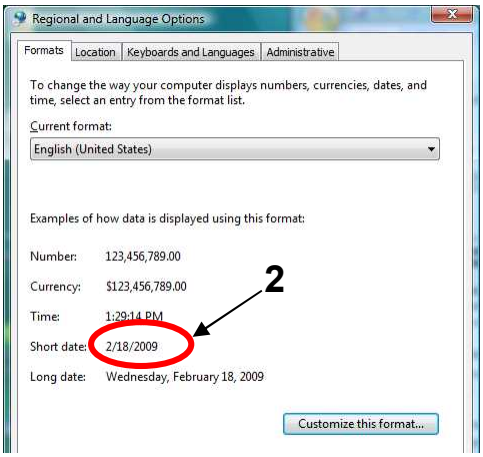


4. Select the "Numbers" tab and change the decimal point symbol to a period ".".

5. Click the [OK] button to store your changes and exit from these settings.

Specifying a date format

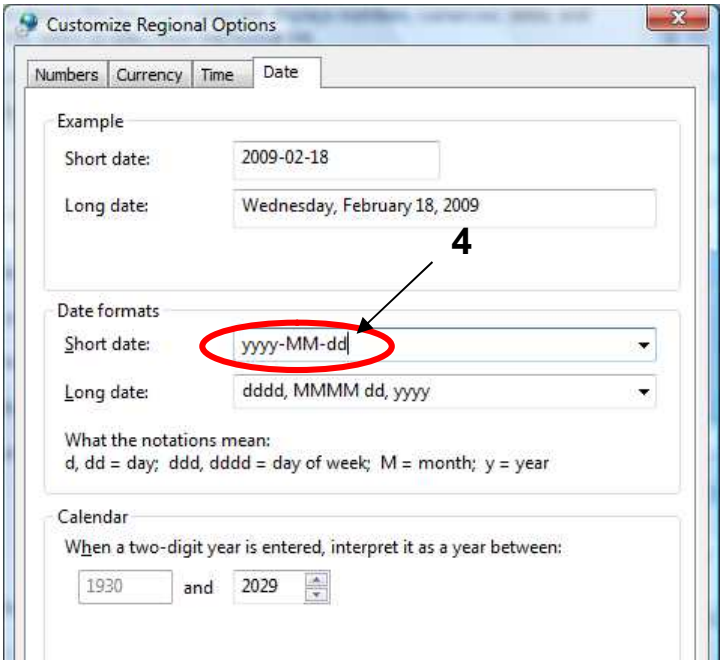
1. In the "Control Panel", select "Regional and Language Options".



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.



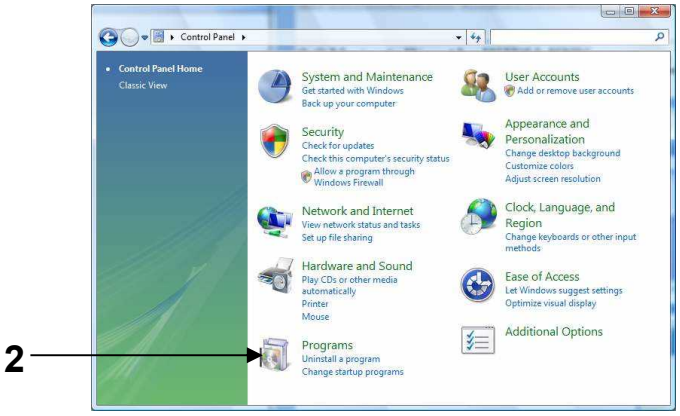
Chapter 3: Uninstalling the analysis program

This chapter describes the steps to uninstall the BELSORP analysis program. First, uninstall the analysis software. After that un-install the WIBU- KEY software.

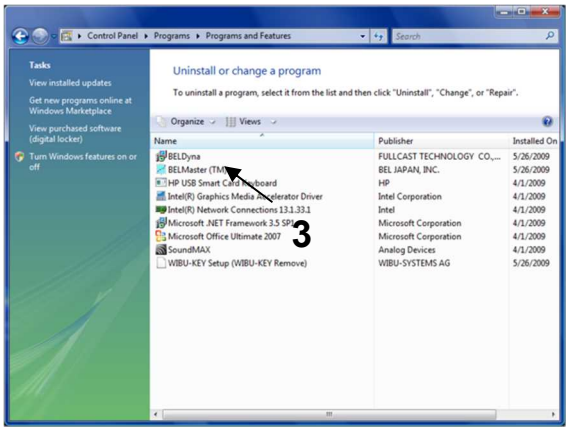
3-1. Uninstalling the analysis program

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.

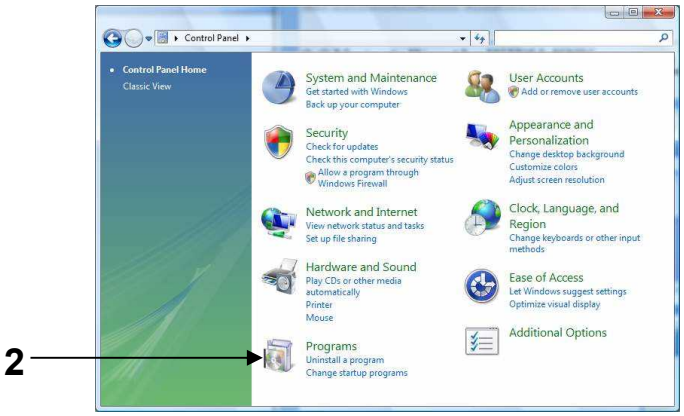
5. Then, your computer may ask you whether or not you really want to delete the shared files. If you are sure there will not be any problem in deleting them, click the [Delete] button. If you are not sure, click the [Save] button. If you are sure you want to delete all the files, click the [Delete all] 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.

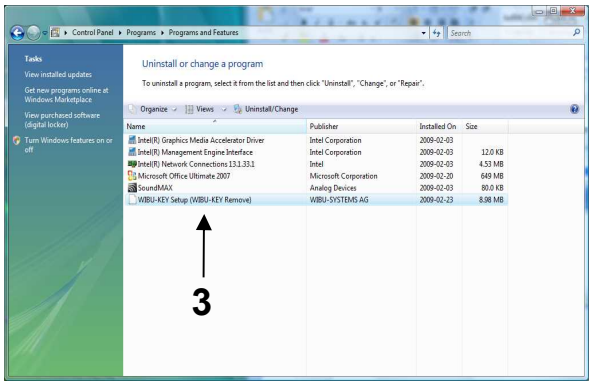
3-2. Uninstalling the WIBU-KEY program

1. Open the Windows “Control Panel”.

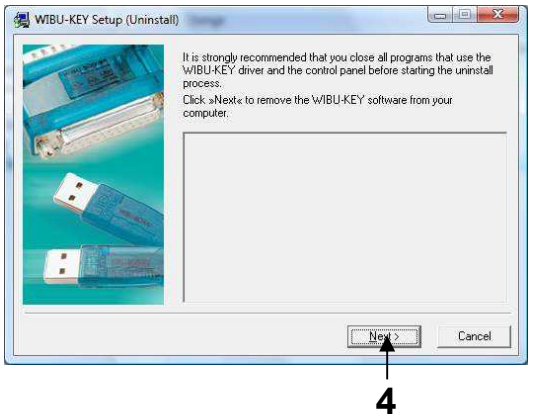
2. Click on the “Uninstall a program”.



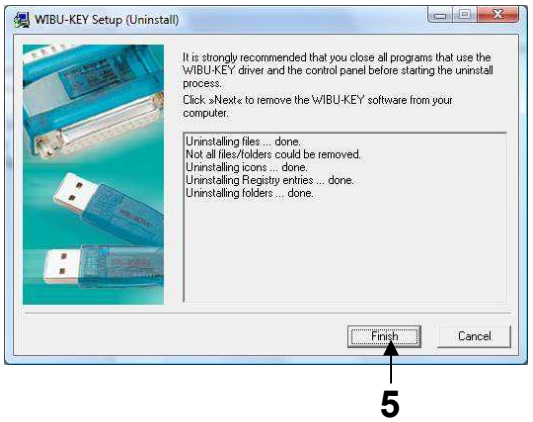
3. Select the “WIBU-KEY Setup (WIBU-KEY Remove)” from the list of programs and click on the [Uninstall/Change] button.



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

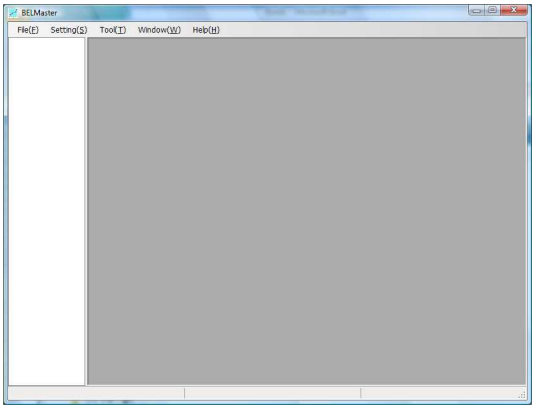
This chapter describes how to start and end the BEL analysis program.
(For details about basic Windows operations, see the Windows instruction manual. Depending on your system's environment, the screen images on your PC may be different from the images shown in this manual.)

4-1. Start up

1. Turn on your computer and start Windows.

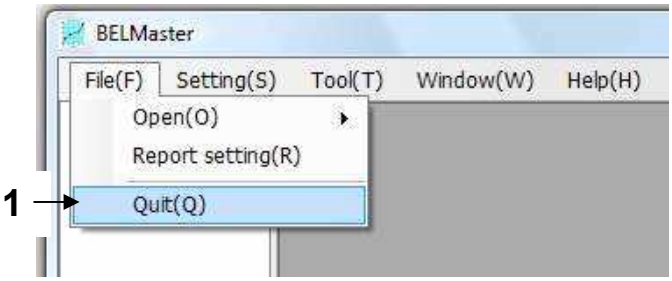
2. From the "Start" bar select "All Programs", "BELSORP" and "Data analysis program" in that order.

3. The BEL analysis program will start and the main window, shown on the right, will appear.

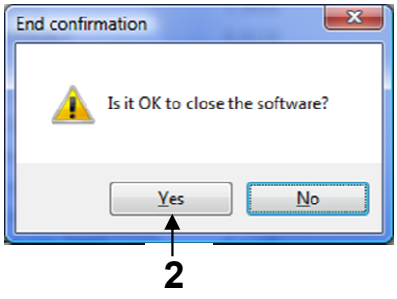


4-2. Quit

1. Select "File (F)" and then "Quit (Q)" from the BEL menu, That will end the BEL analysis program.



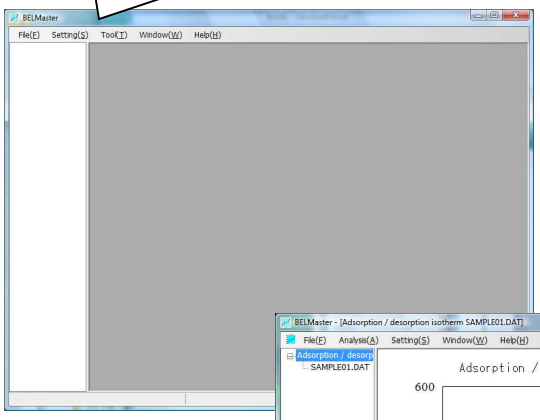
2. After the dialog box appears as shown on the right, select "Yes (Y)".



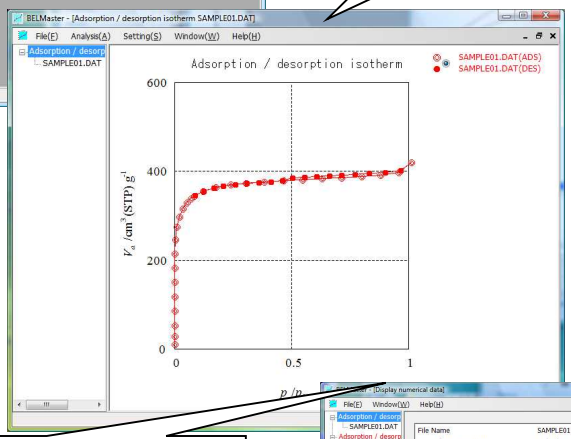
Chapter 5: “Main” window

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.

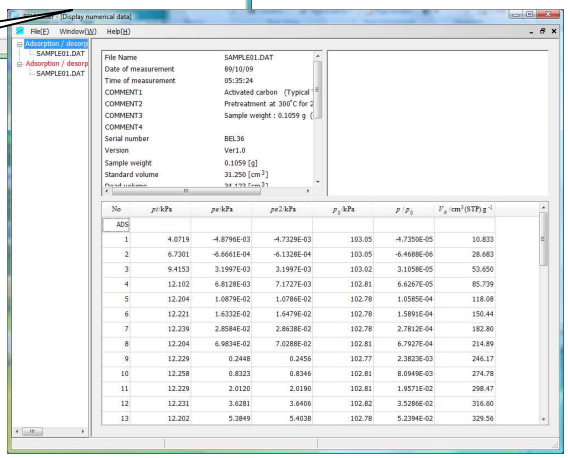
5-1. Initial menu
(The first menu displayed after starting the BEL analysis program)



5-2. Menu while analyzing data
(When the data is being displayed as a graph)

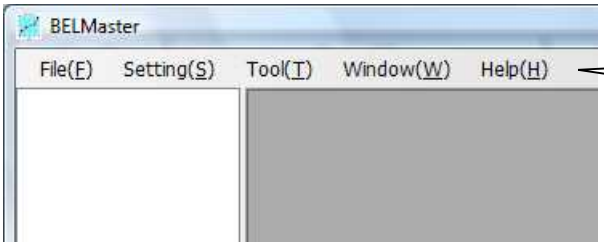


5-3. Menu while analyzing data
(When the data is being displayed as the numerical data)



5-1. Initial menu

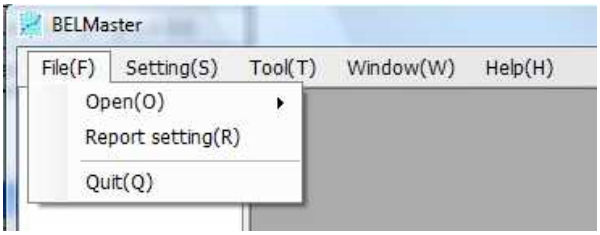
1) Menu contents



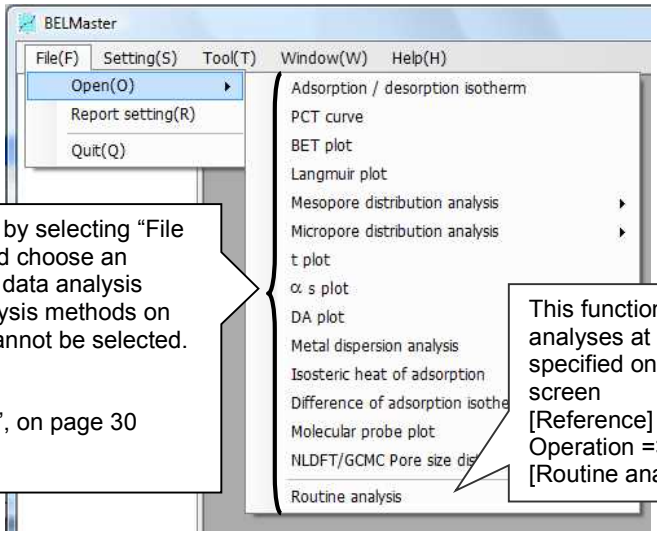
The first menu displayed after starting the BEL analysis program (no data file is open)

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



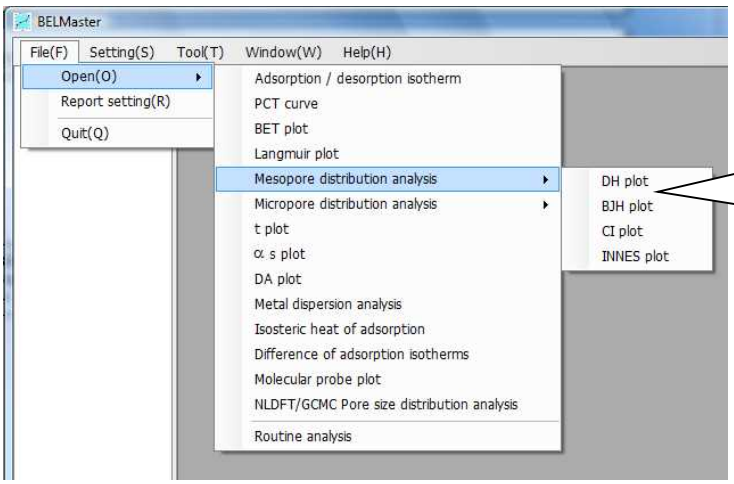
- "Open (O)" menu

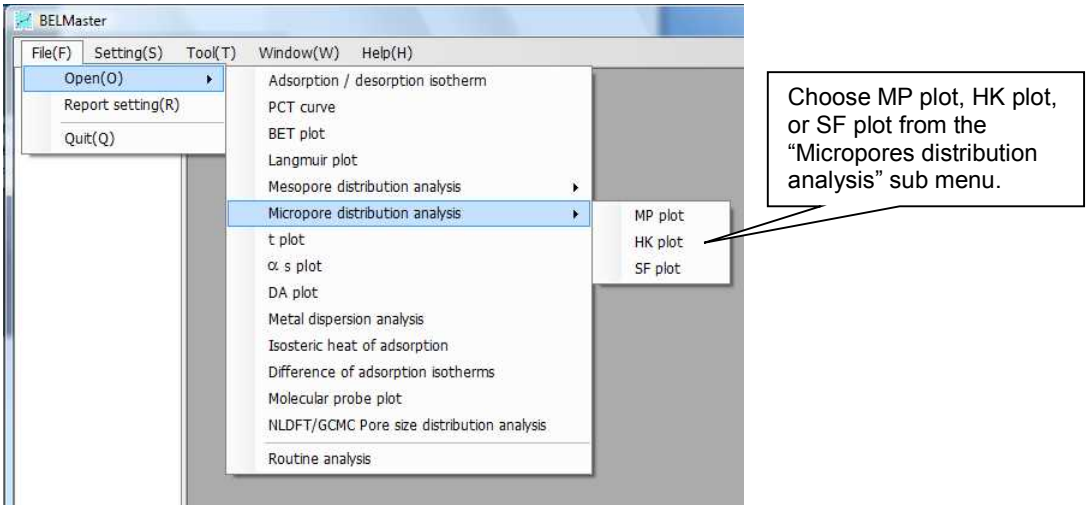


Open the data analysis window by selecting "File (F)". Then select "Open (O)" and choose an analysis method. The graphic data analysis screen will be displayed. Analysis methods on the menu that are grayed out cannot be selected.

[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.

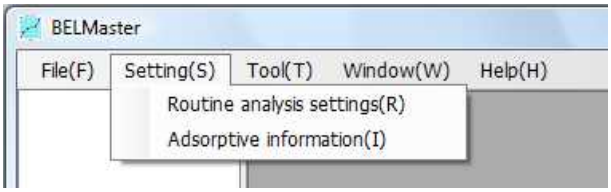
[Reference]
Operation => Chapter 31: Output an analysis report, on page 145.

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)

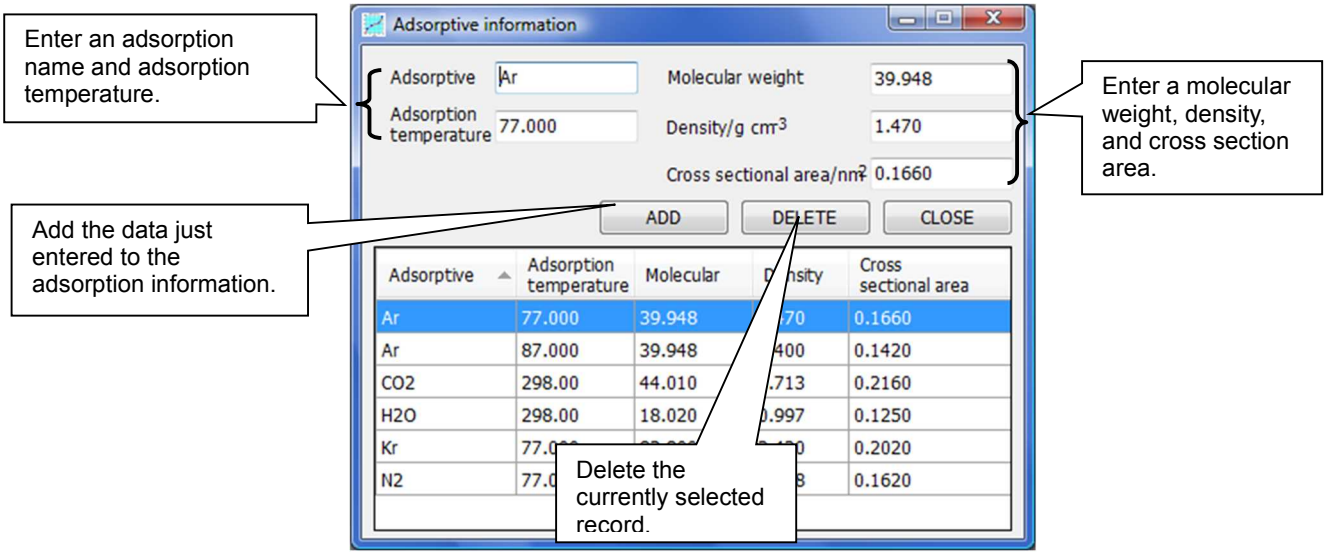
Specify the analysis methods to execute in a routine analysis.

[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/

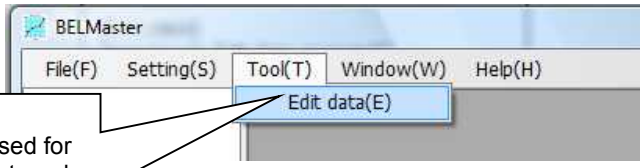
*4 Chemistry handbook basic 4th edition, Chemical Society of Japan, Maruzen Co., LTD.

*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

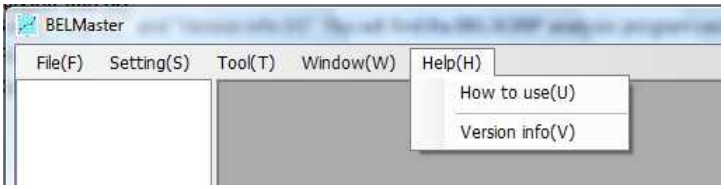
- “Edit data (E)”



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)”

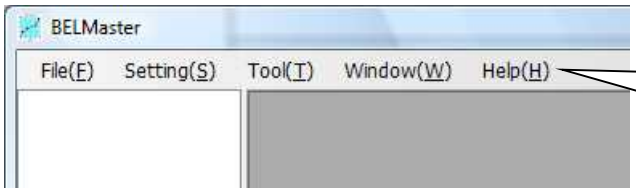
Select “Help (H)” and “How to use (U)”. The BELMaster manual can be refer here.
[Reference]
Operation => How to use the analysis program, on page 55.

- “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)

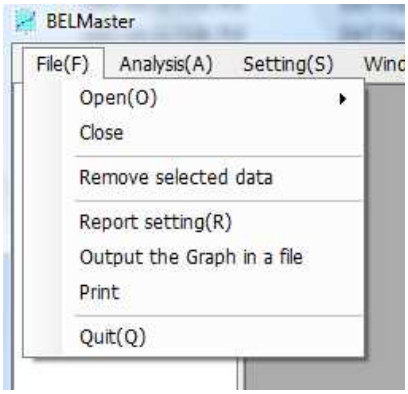
1) Menu structure



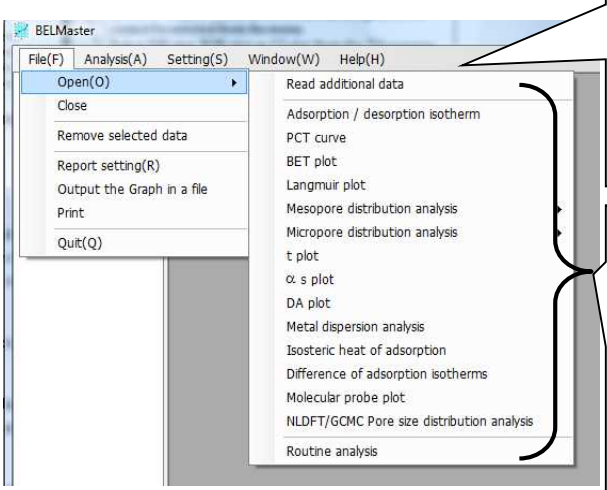
While analyzing data (more than one data set is open), this menu will appear when the active data analysis window is a graph.

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"

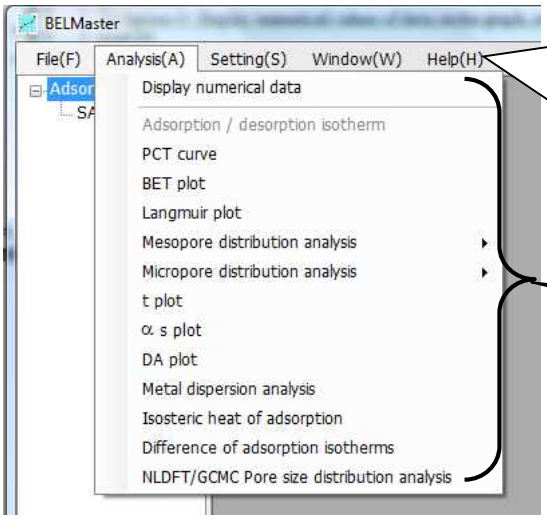
Select "File (F)" and "Print". Then you can print a data analysis graph of the active analysis window.
[Reference]
Operation => Print data analysis (graph), on page 51

- "Quit"

Select "File (F)" and then "Quit (Q)" to end the BEL analysis program.

3) "Analysis (A)" menu

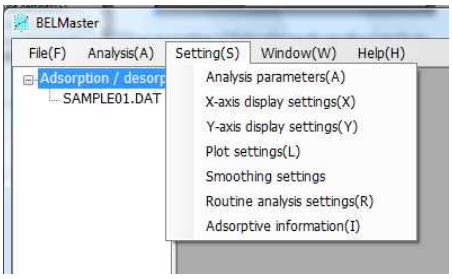
The "Analysis (A)" menu is not displayed if the Molecular probe method analysis window is active.

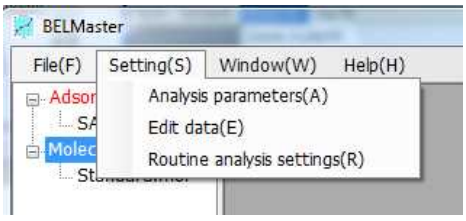


If you select "Analysis (A)" and then "Display numerical data", the program will open a new data analysis window and show you the numerical data. It will display numerical data for the active data (data whose check box has been selected) in the currently active window.
[Reference]
Operation => Display 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



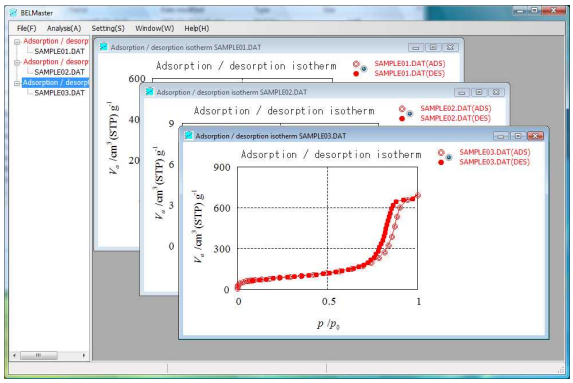


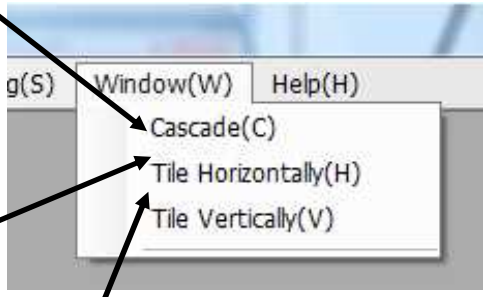
When executing a Molecular probe method analysis.

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

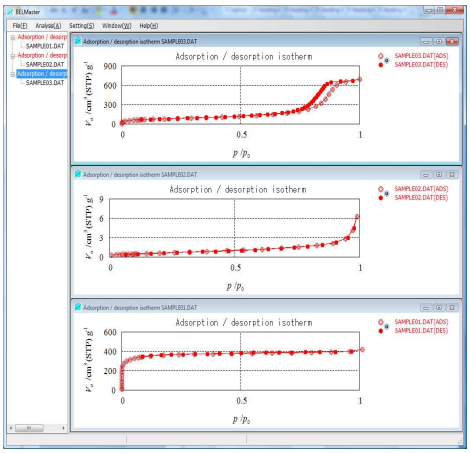
5) "Window (W)" menu

Select "Window (W) " and then "Cascade (C)".
Multiple windows are displayed by overlapping them.

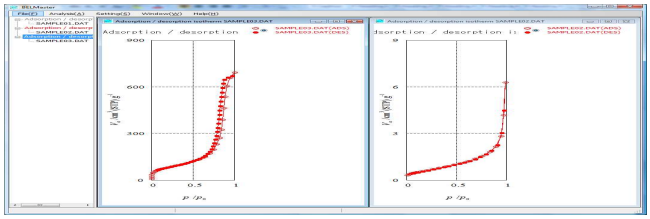




Select "Window (W)" and then "Tile Horizontally (H)". The program will display the windows arranged horizontally.



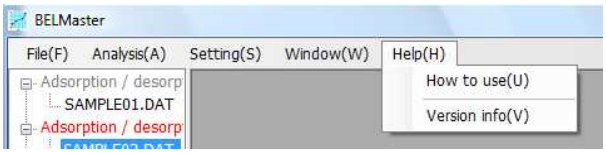
Select "Window (W)" and then "Tile Vertically (T)".
The program will display the windows arranged vertically.



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.

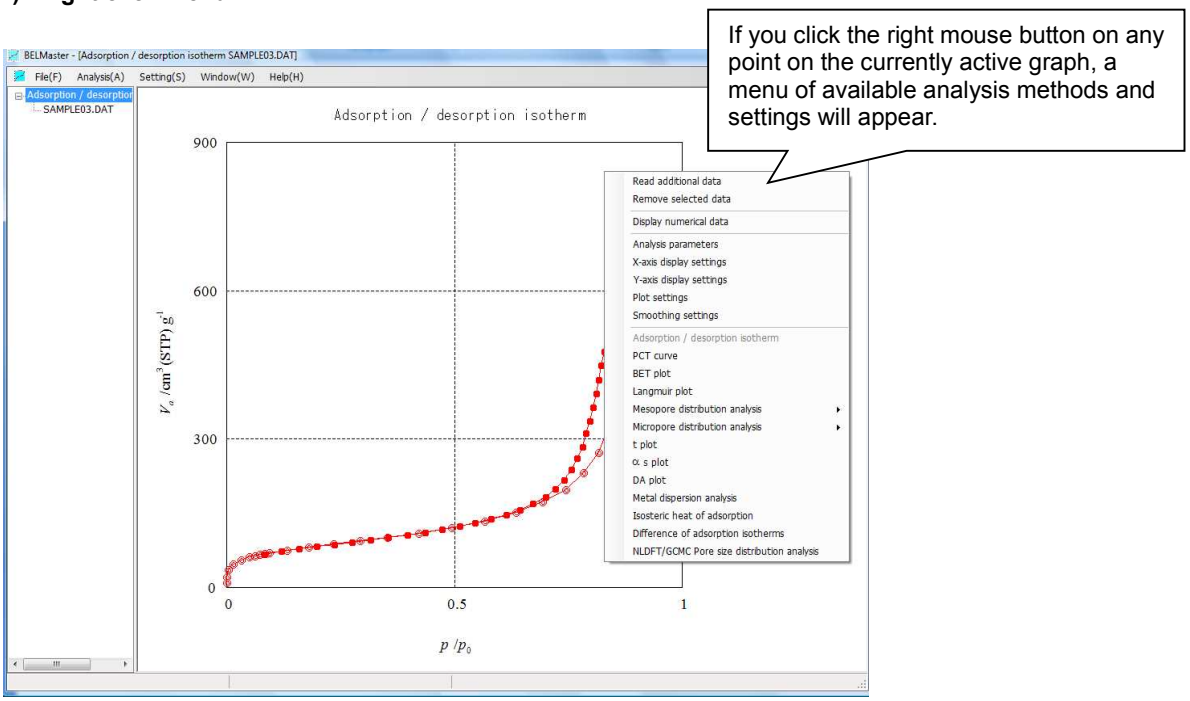
- "Version info (V)"

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.

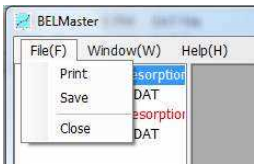
[Reference]

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

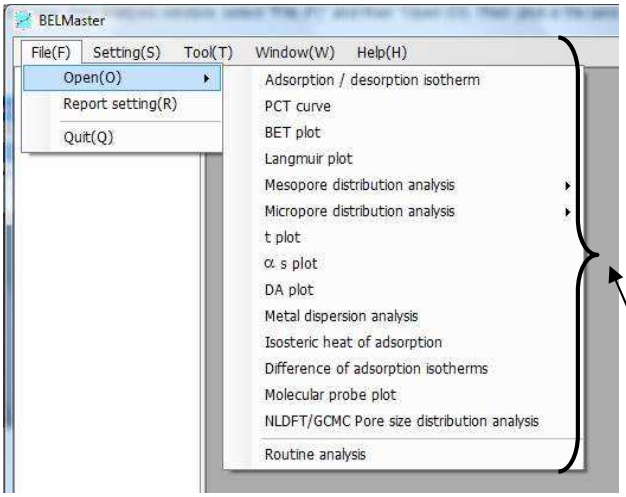
This chapter describes how to read in data that were measured by BELSORP series apparatuses, and how to display the graphis and numerical.

6-1. “File open”

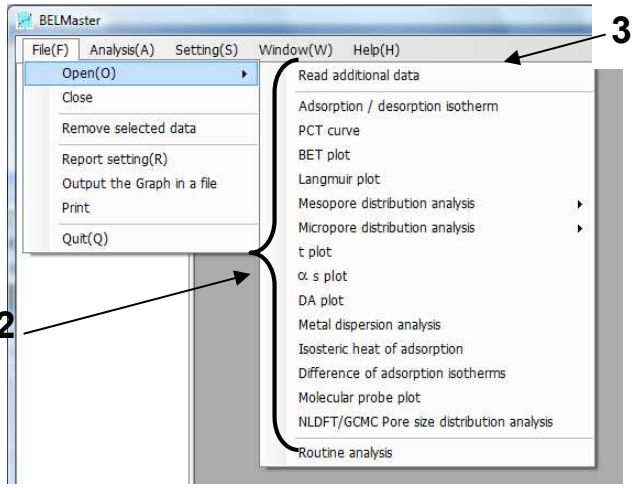
1. The following methods can be used to select a data analysis file.
   Reading data into a new data analysis window
   - Select from the analysis program menu 2

   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).



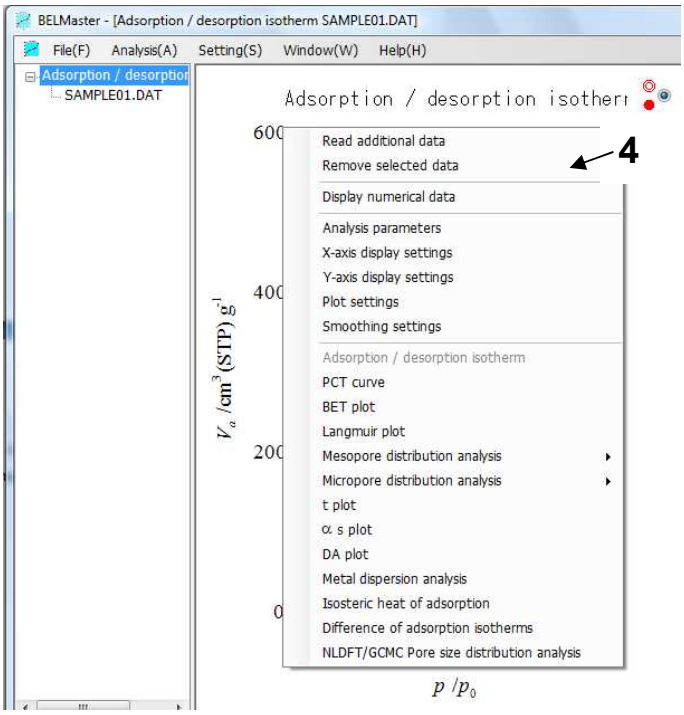
Initial menu



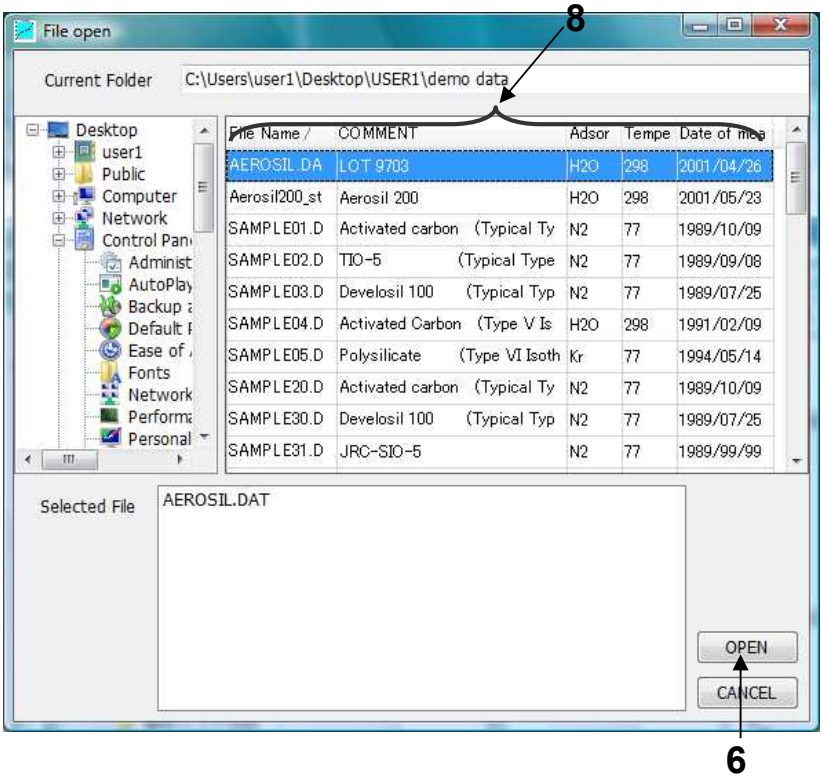
Menu while analyzing data

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.

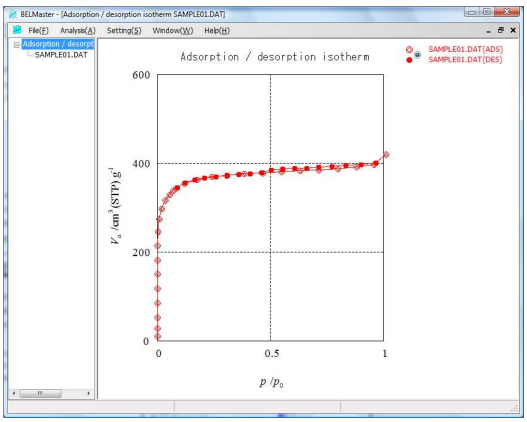


5. After step 2, 3 or 4, the “File open” window shown below will appear.



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.

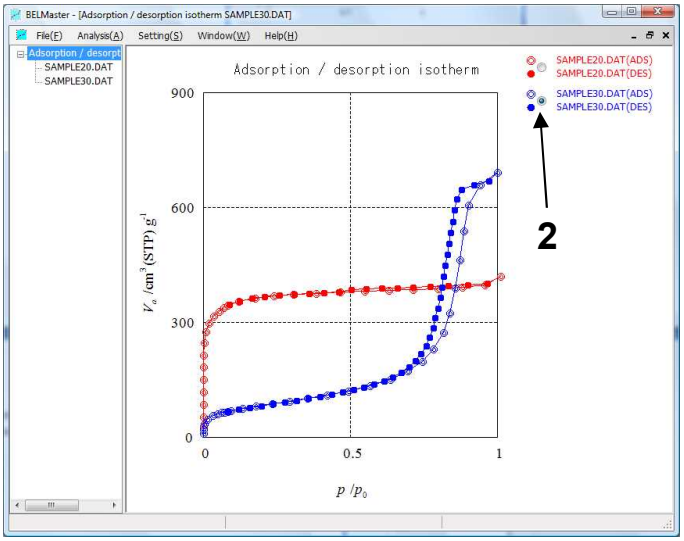


8. To change the order in which data is listed, click on the name of an item on the top line, such as “File name” or “comment name”. The program will sort the list according to the selected item. An up arrow “△“ on the left of the item name means that the data are displayed in ascending order. A down arrow “▽“ on the left means that the data are displayed in descending order.

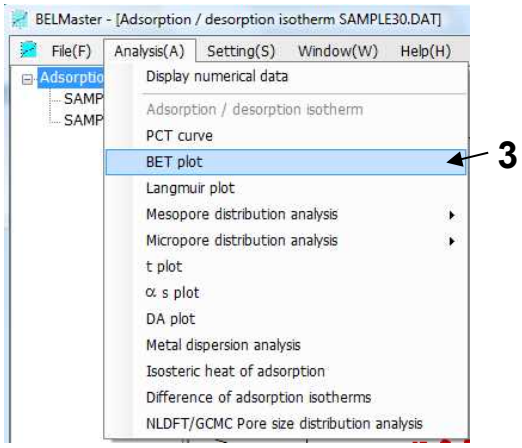
6-2. Analysis of active data (graph)

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

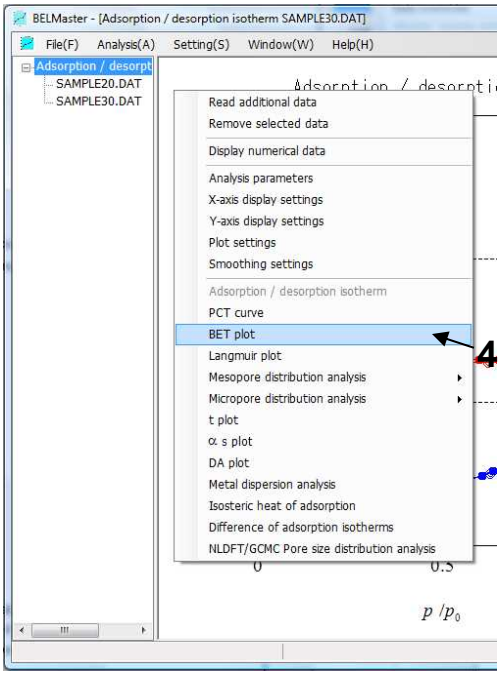
2. Select the data you want to analyze. If more than two data curves are drawn in a window, check the box for data you want to analyze.



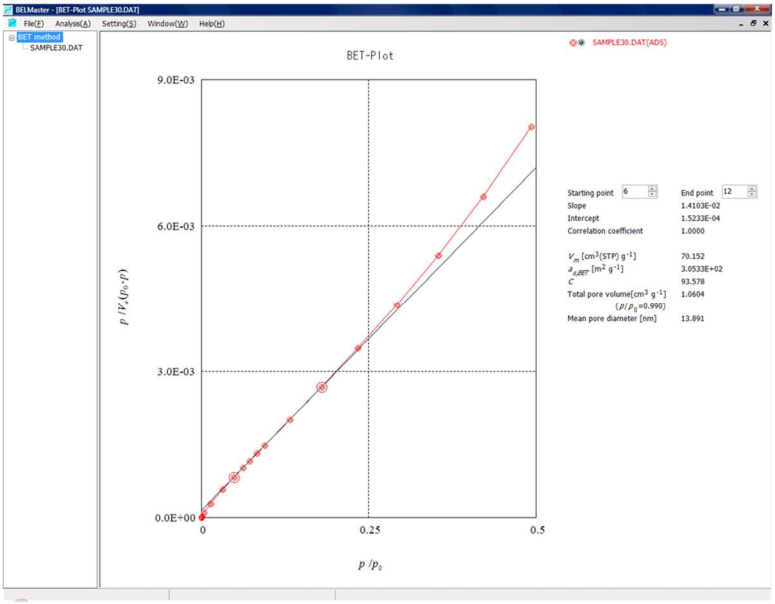
3. Select “Analysis (A)” and then an analysis method from the “Analysis” method menu.



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”.



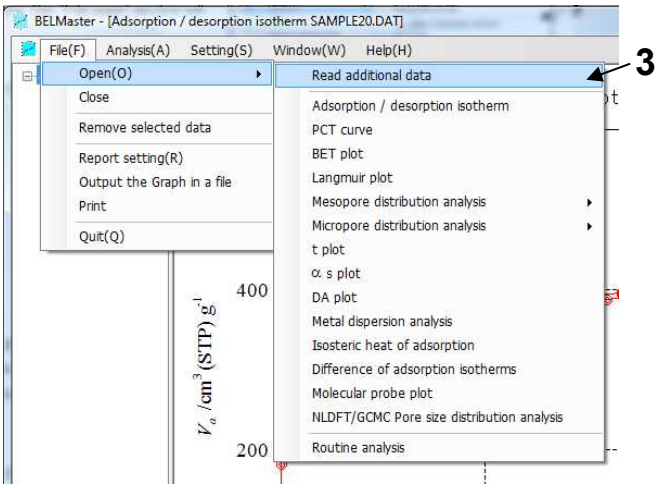
6-3. Adding data files to the active window (graph)

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

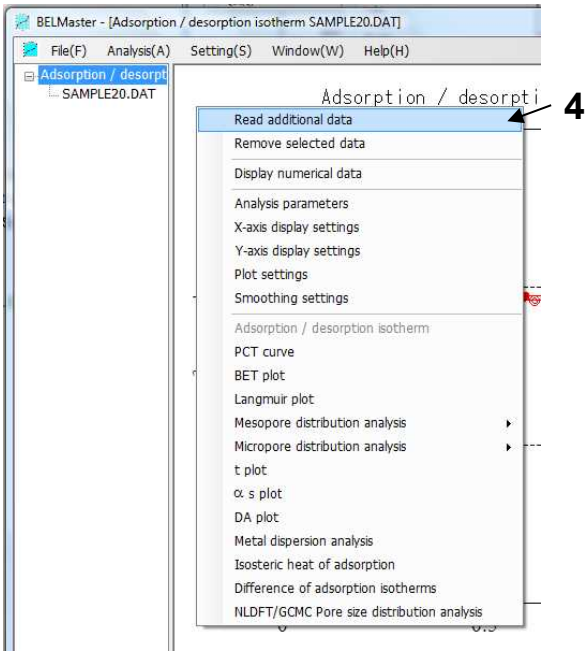
2. Click on the data analysis window you want to add to, to make it active.

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.

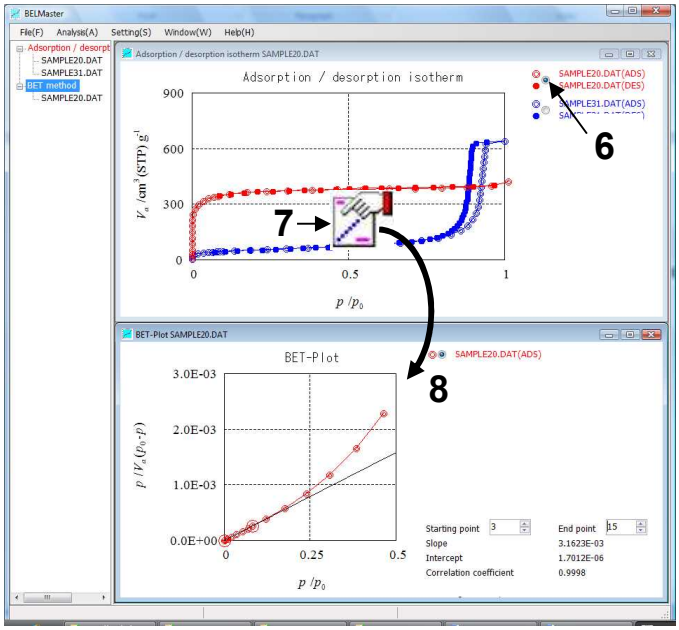


5. You can add data from another data analysis window to the current graph by dragging and dropping.

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.

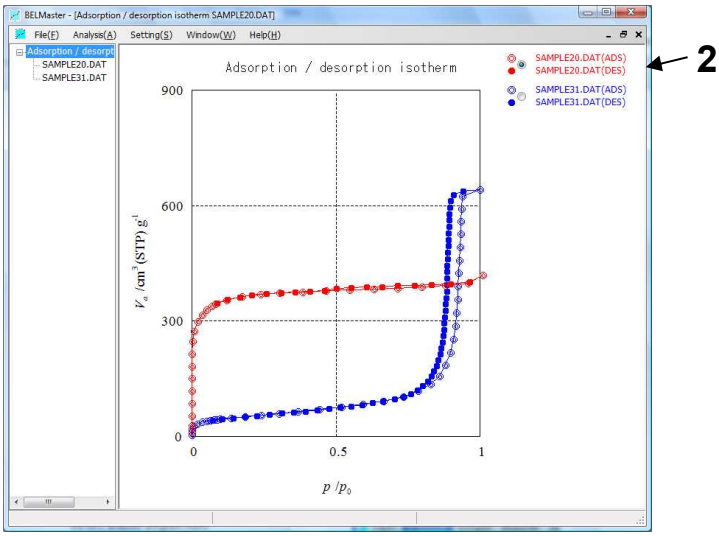


9. After analyzing data using a specified analysis method, the program displays this data overlapped on the graph.

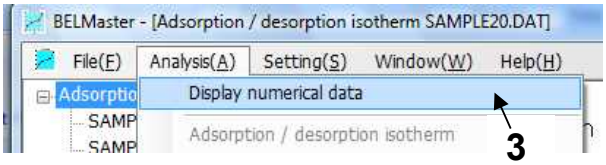
6-4. Display the numerical values of data on the graph

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

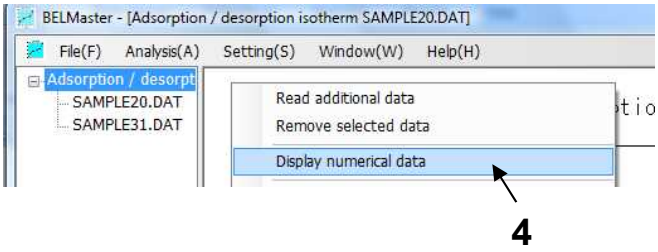
2. Select the data set you want to display as numbers. If more than two data sets are drawn on a window, check the box for the data you want to display.



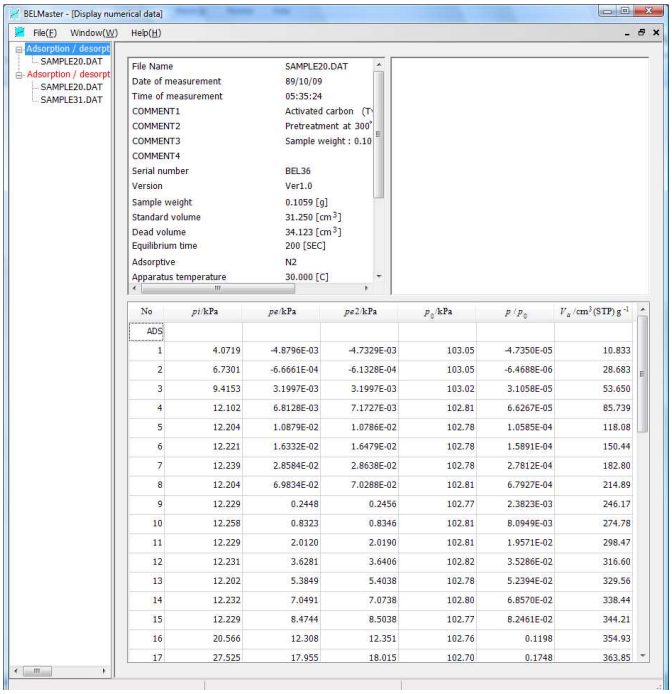
3. Select “Analysis (A)” and then “Display numerical data” from the BEL analysis program menu.



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.



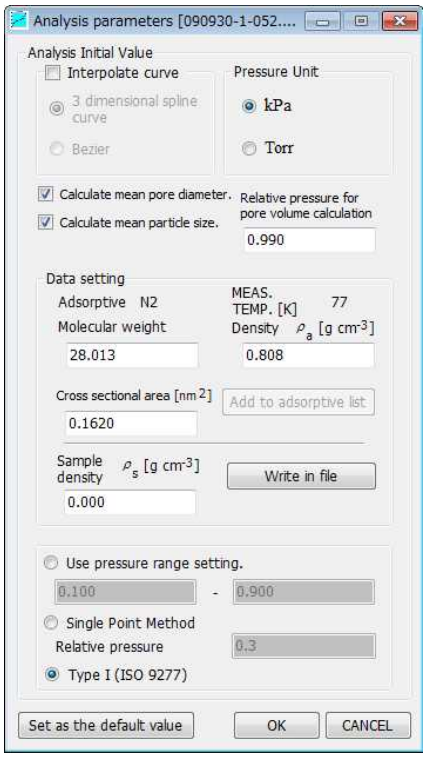
Chapter 7: “Setting” window

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.

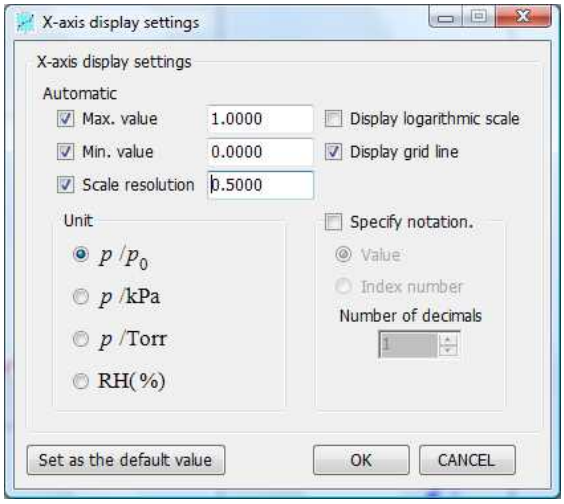
Adsorptive molecular weight	Enter the molecular weight of the adsorptive
Cross sectional area	Enter the Cross sectional area [nm^2]
Adsorptive density	Enter the density [g cm^{-3}] of the adsorptive
[Add to adsorptive list] button	If the adsorptive name does not exist and the adsorption temperature is 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.

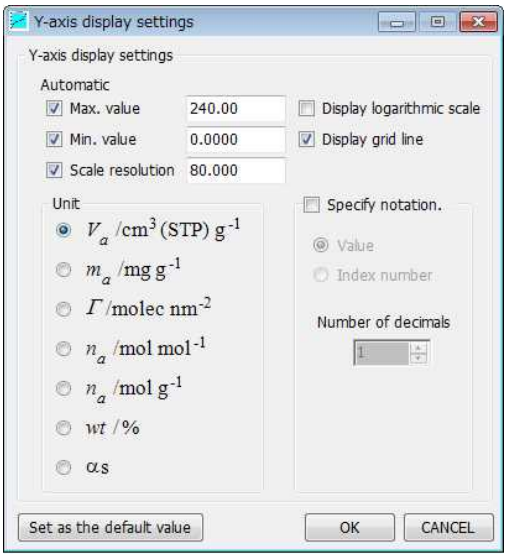
Automatic	Switch between auto/manual for the maximum and minimum values and the scale resolution of an axis.
Setting input box	When you want to enter the maximum, minimum, and scale resolution manually, change [Autmatic check box] by clicking off it. Then enter the values as numbers.
Unit	Select the 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.



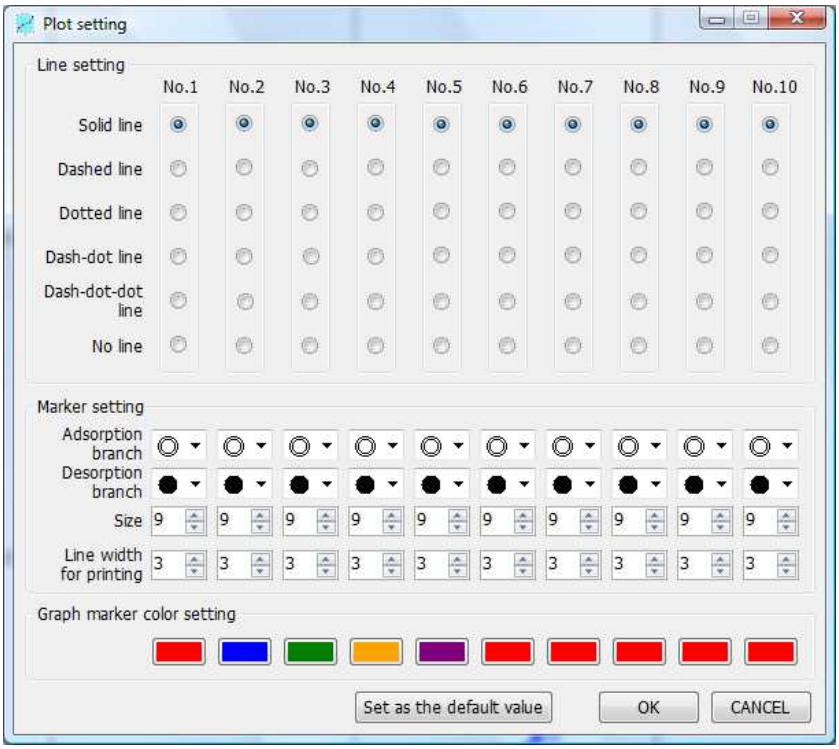
“Y-axis display settings” window for adsorption isotherm.

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”.

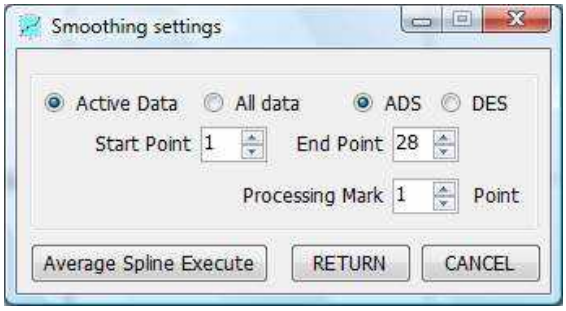


“Plot setting” window

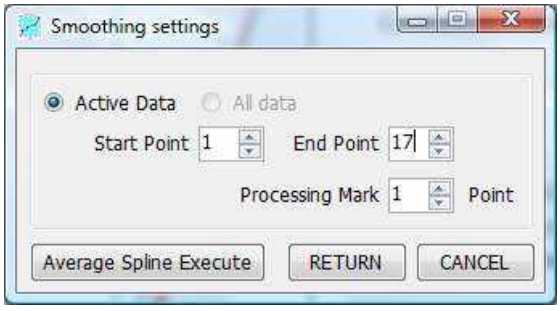
Line setting	Select the line type for data No. 1 to 10.
Line width for printing	Select the line thickness to use when printing.
Adsorption branch	Select the data point marker for the adsorption side.
Desorption branch	Select the data point marker for the desorption side.
Size (marker size)	Set the marker size.
Graphic marker color setting	Select the colors used for markers and lines.

7-5. Smoothing settings

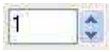
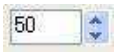
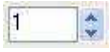
The selected data analysis results can be smoothed with these settings.



"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

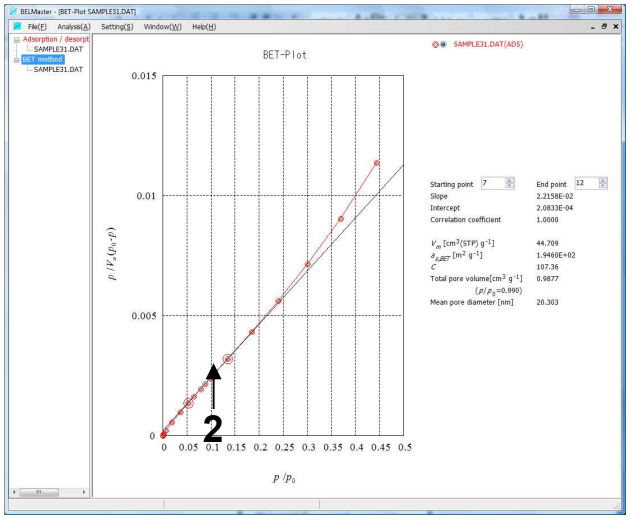
A “graphic” window and a “numerical value data” window are available to display the data analysis. This chapter describes the operations common to the “graphic” window. For details about operations specific to each analysis method, see Chapters 11 to 31.

8-1. Display plot data details

You can display coordinates of the plot data on a graph using the procedures below.

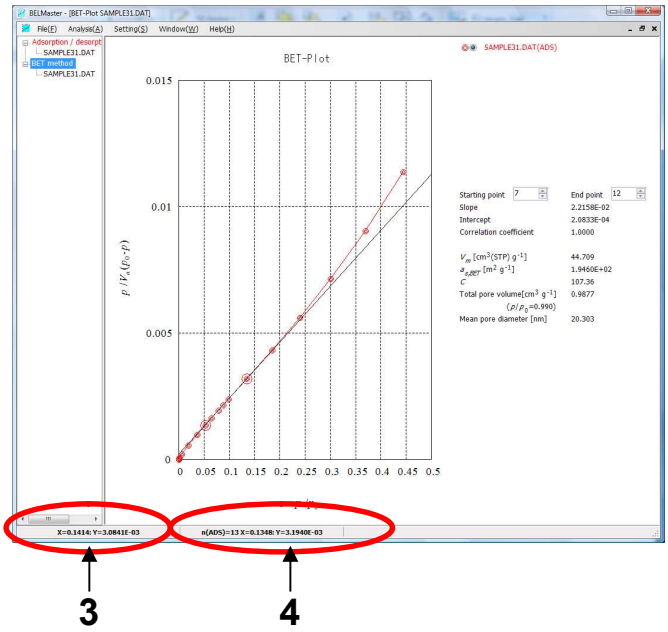
1. Select the plot data to display. When more than two data curves are displayed on the same graph, click the check box of each data set whose coordinates you want to display.

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.

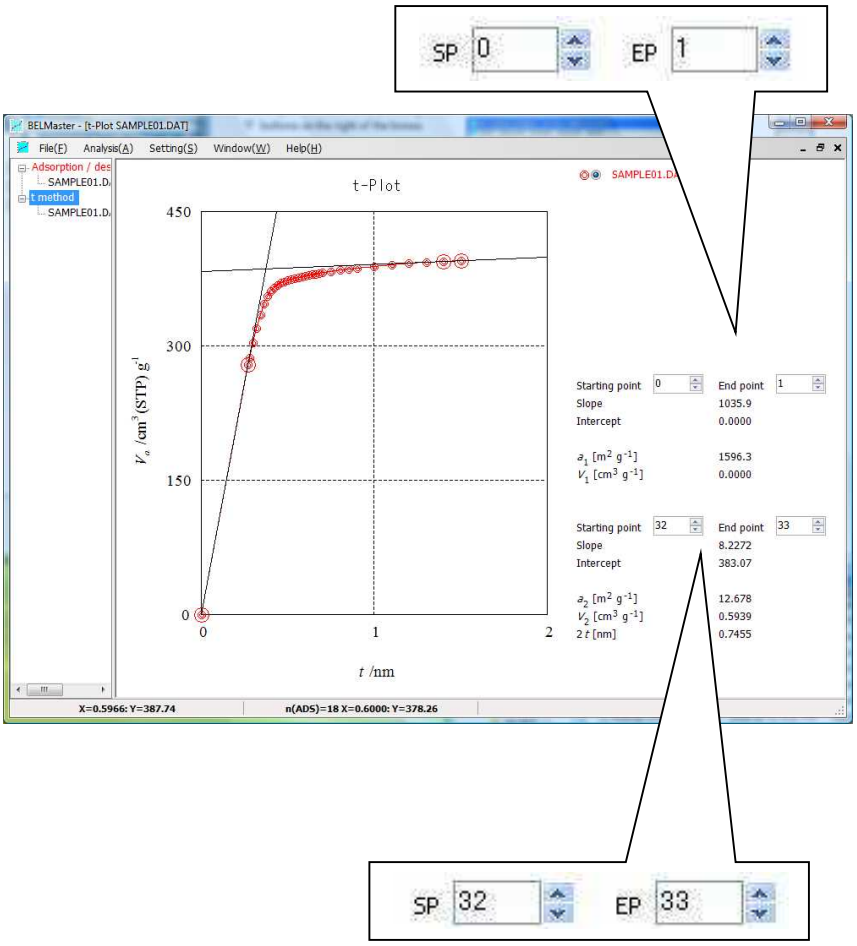


8-2. Setting the linear regression start and end points.

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.

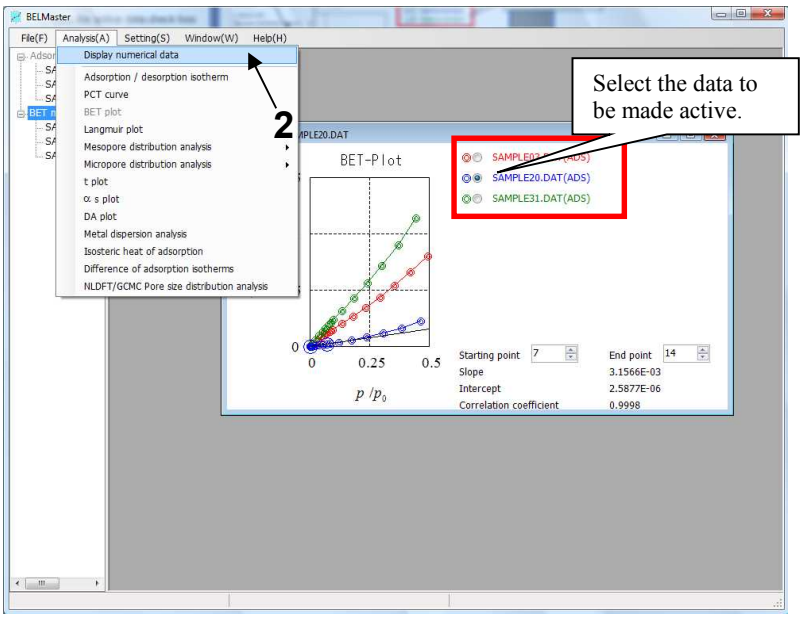
2. By changing these values, you can change the objective linear regression range. The numbers can be changed by entering a new value or by pressing the △▽ buttons on the right of the boxes.

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

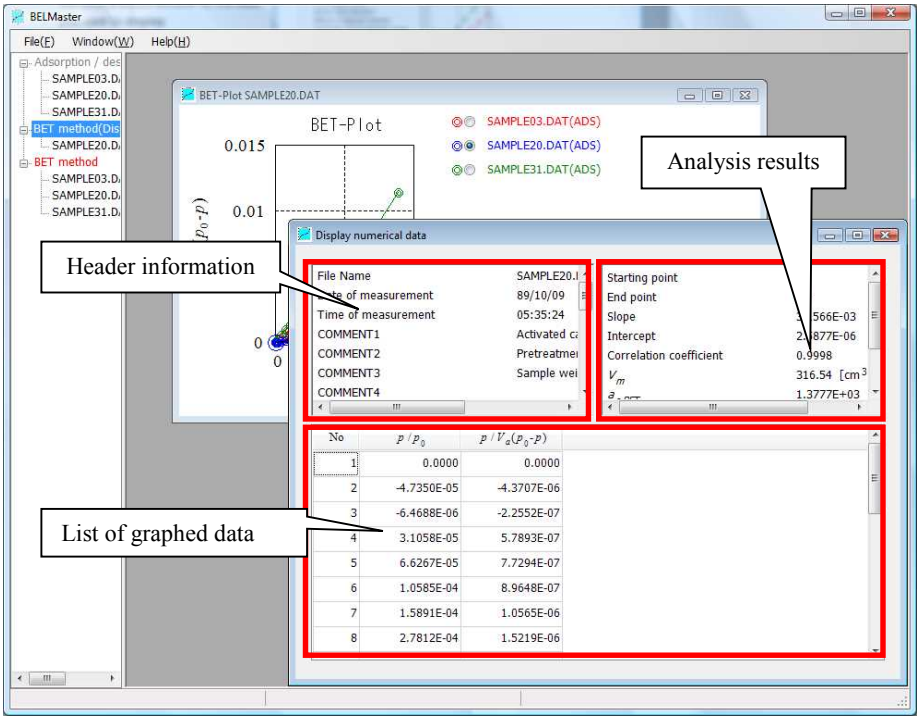
This function displays the numerical data for the graph data currently being analyzed.



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.

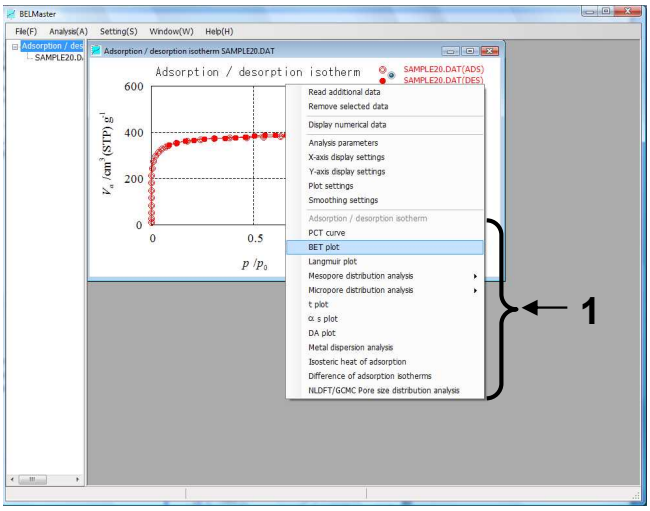
3. A new data analysis window will open and a list of the active data and header information will be displayed.



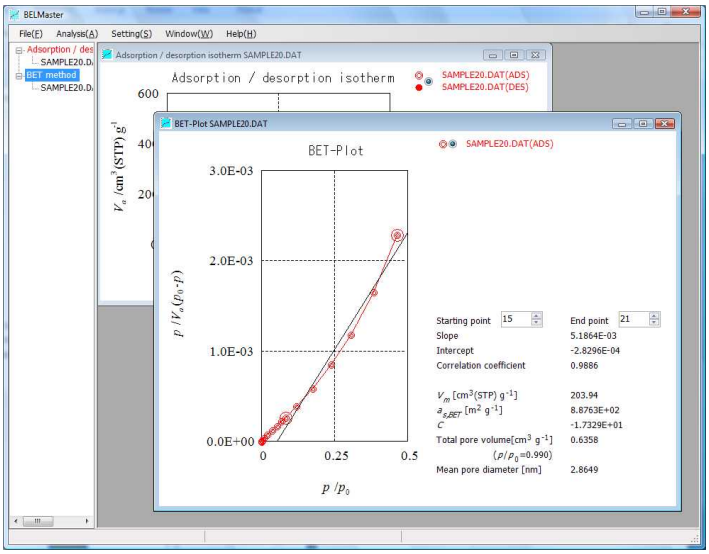
8-4. Analyze the active data by using another analysis method

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.

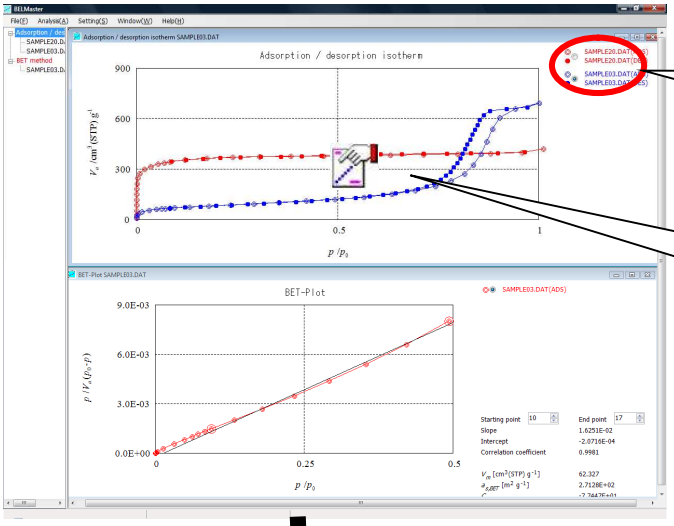


2. After selecting an analysis method, a new data analysis window will open. The program starts analysis of the data specified in the original graph. The figure below shows the results of executing a "BET analysis" from an "Adsorption / desorption isotherm".



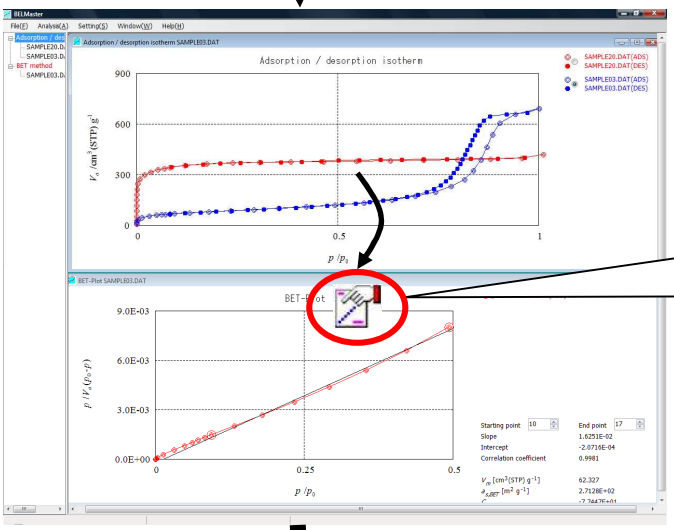
8-5. Transfer the data using the drag and drop function

When a data analysis window is already open, you can transfer the data by dragging and dropping the graph data.

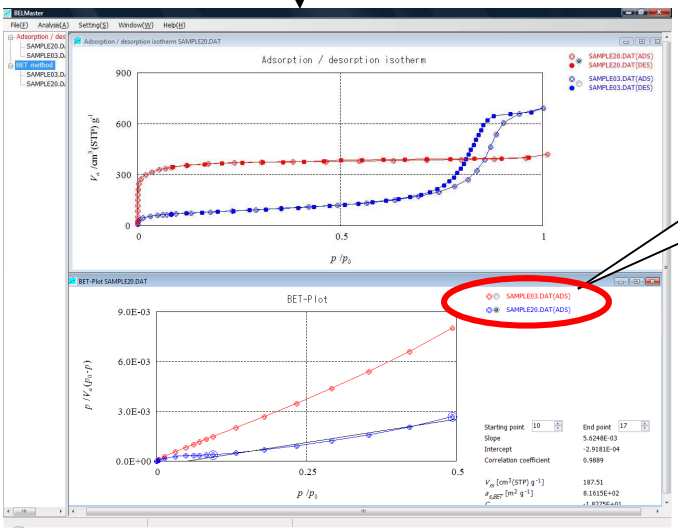


1. Confirm that data you want to transfer has been selected.

2. Move the cursor on the graph while holding down the left mouse button (The icon will change.).



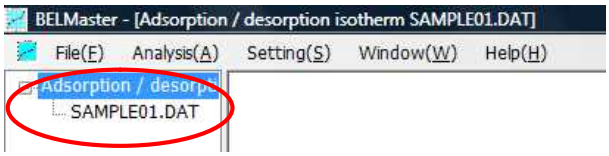
3. Move the cursor to the data analysis window you want to transfer data to while holding down the left mouse button. Then, release the left mouse button.



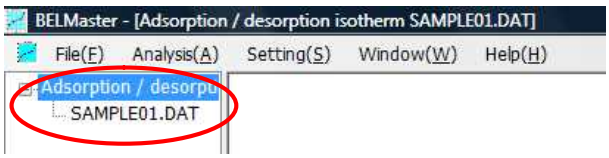
4. The data and graph will be added to that window.

8-6. Displaying the sub screen

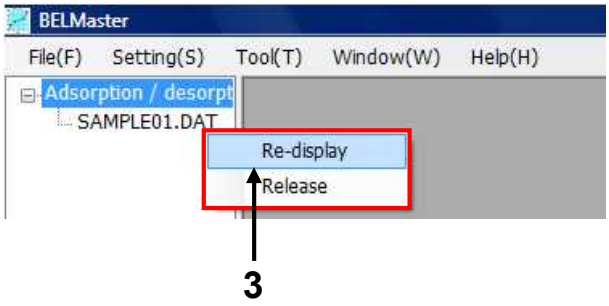
1. The file name for the currently analyzed graph data is displayed on the sub screen.



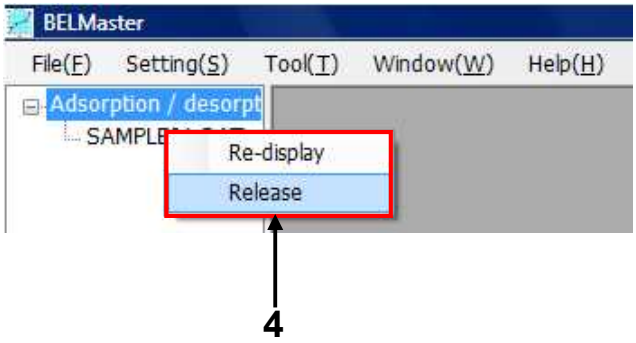
2. Even after graph data is deleted from the main screen, the analysis method and file name will be retained. (If you execute “Delete”, the analysis method and file name on the sub screen will be deleted.)



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.

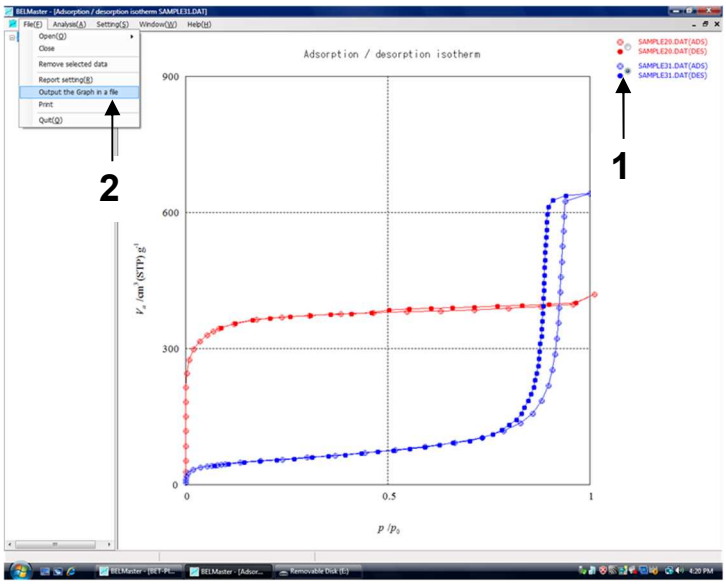
9-1. Save data analysis

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.

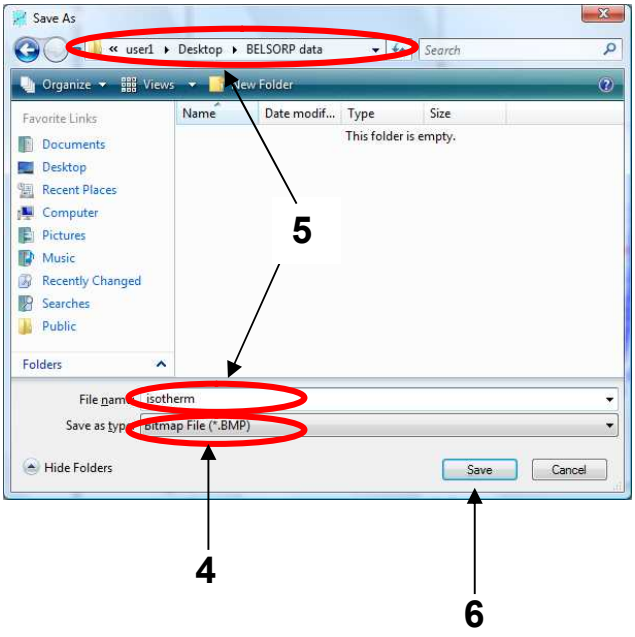


3. The “Save As” window shown on the right will appear.

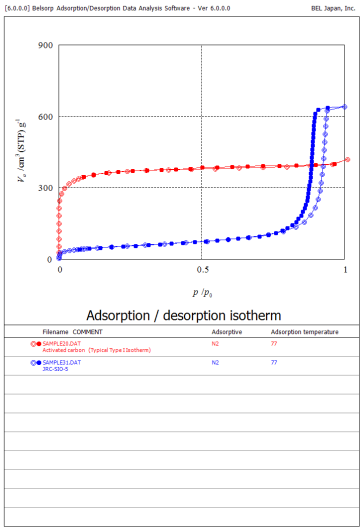
4. Select a file type (Bitmap File / Meta File).

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.



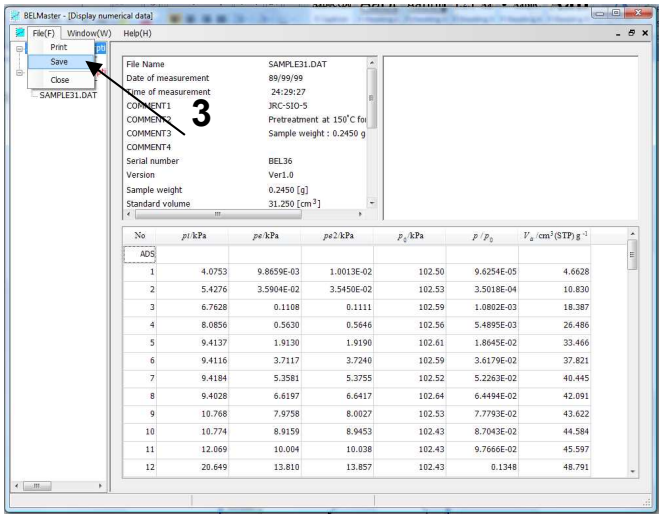
2) Save a data analysis (numerical data)

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.



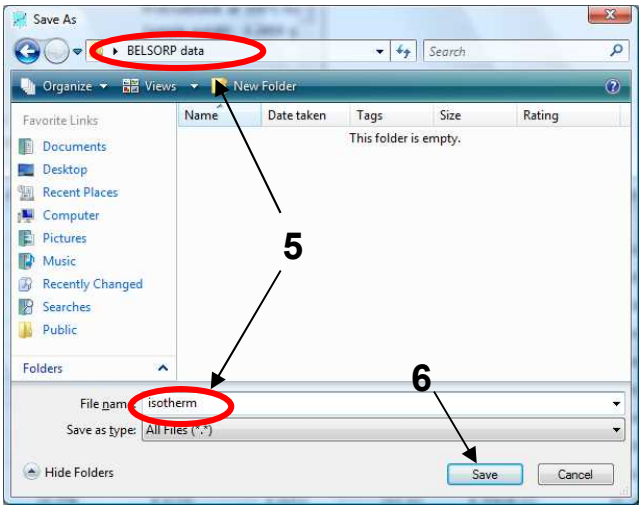
2. Select the analysis window that is displaying the numerical data to save.

3. Select “File (F)” and “Save” from the BEL analysis program menu.

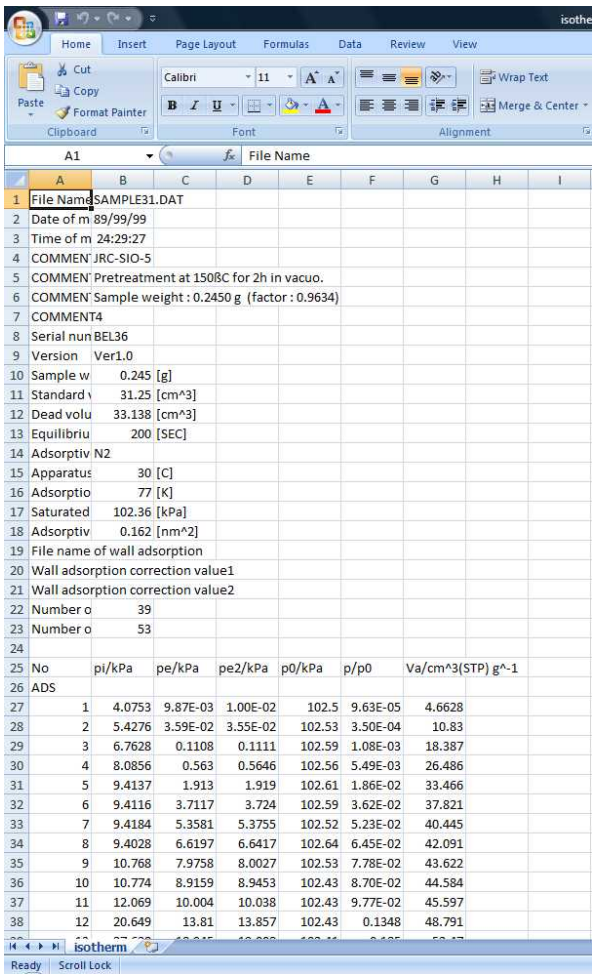
4. The “Save As” window shown on the right will appear.

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		

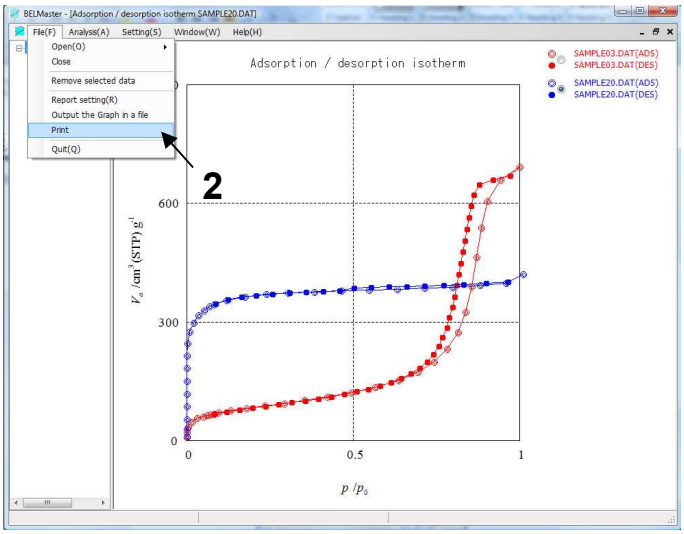
9-2. Printing a data analysis

1) Print a data analysis (graph)

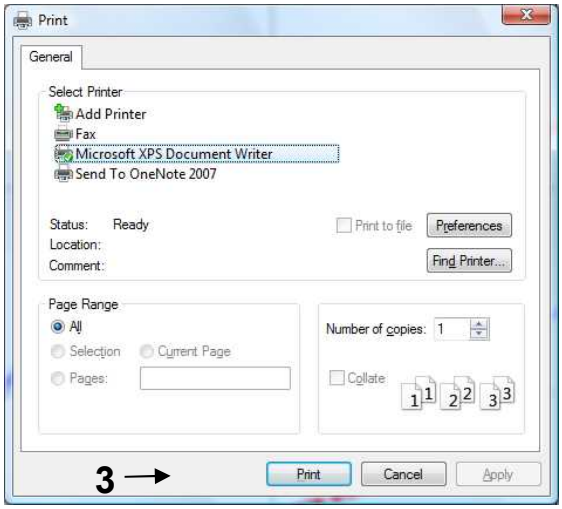
A graph of a data analysis can be printed on paper.

1. Select the analysis window containing the graph you want to print.

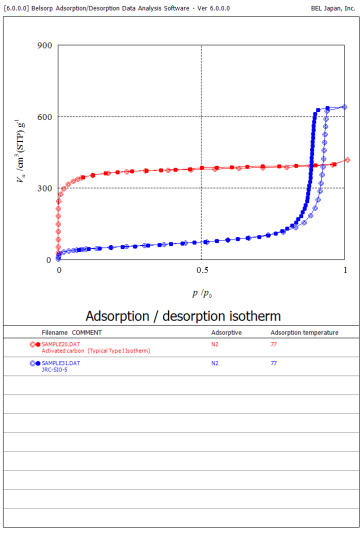
2. Select “File (F)” and “Print” from the BEL analysis program menu.



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.

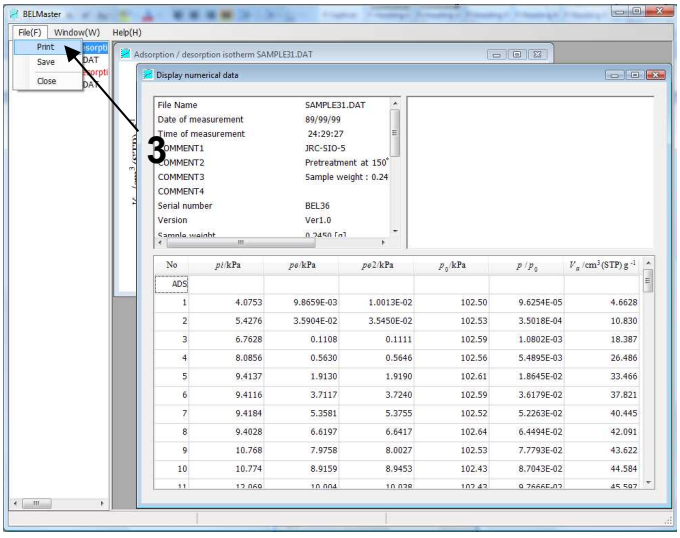
1. Display the numerical data you want to print.

[Reference]

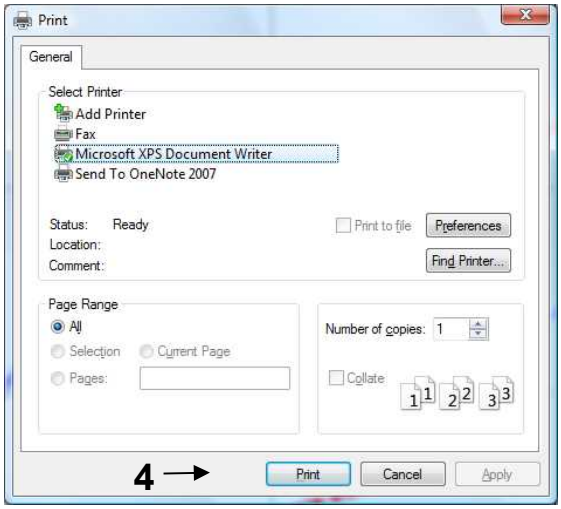
Display numerical data => Display the numerical data from a graph, on page 35.

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

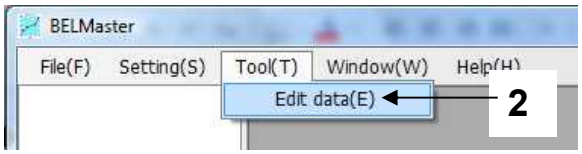
No	p_i /kPa	p_e /kPa	p_{e2} /kPa	p_0 /kPa	p / p_0	V_a /cm^3(STP) g^{-1}
1	4.0753	9.8659E-03	1.0013E-02	102.50	9.6254E-05	4.6628
2	5.4276	3.5904E-02	3.5450E-02	102.53	3.5018E-04	10.830
3	6.7628	0.1108	0.1111	102.59	1.0802E-03	18.387
4	8.0856	0.5630	0.5646	102.56	5.4895E-03	26.486
5	9.4137	1.9130	1.9190	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.



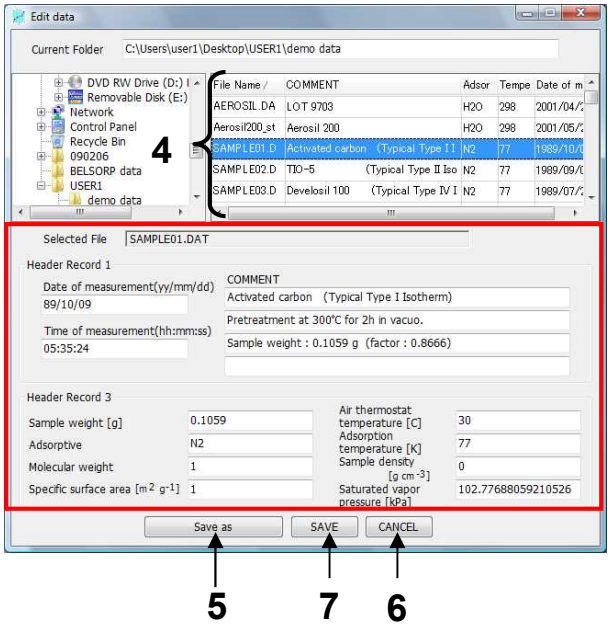
3. The “Edit data” window shown on the right will appear.

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.

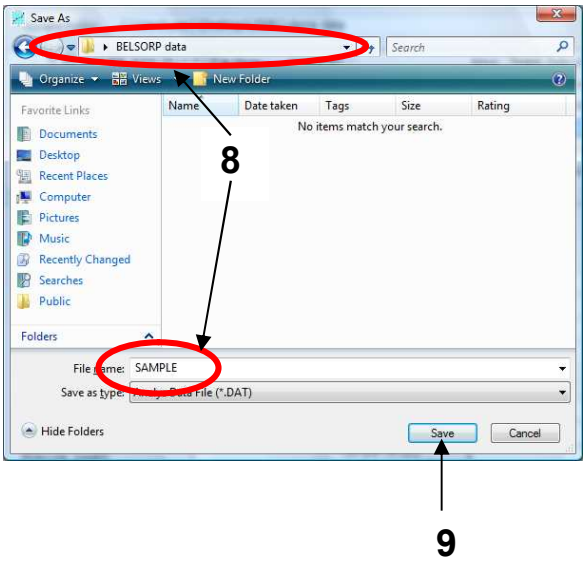
6. If you want to overwrite the existing file, click the [SAVE] button. An overwrite message window will appear. Select [Yes] and the program will overwrite the items that you changed.

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.

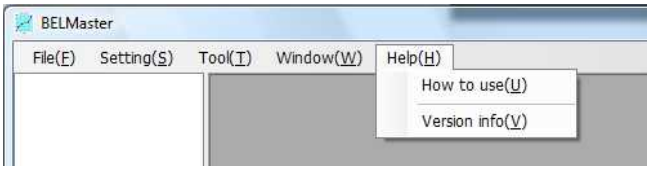


9-4. Help function

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.

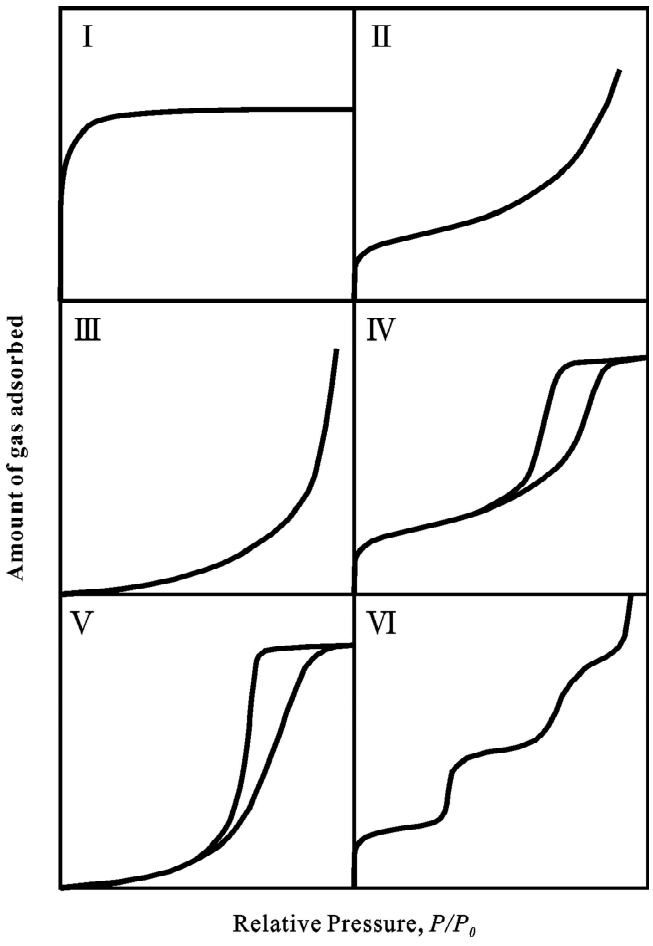


Figure 1: IUPAC classification of adsorption isotherms

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.

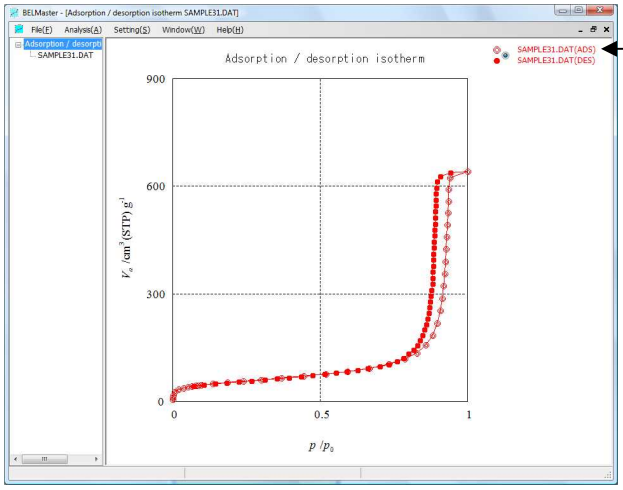
*7: "*wt/%*" is percentage of weight of adsorption per gram of sample.

*8: A value obtained by dividing an adsorption amount at arbitrary equilibrium pressure by adsorption amount *Va (p/p0 = 0.4)*

11-2. Operation

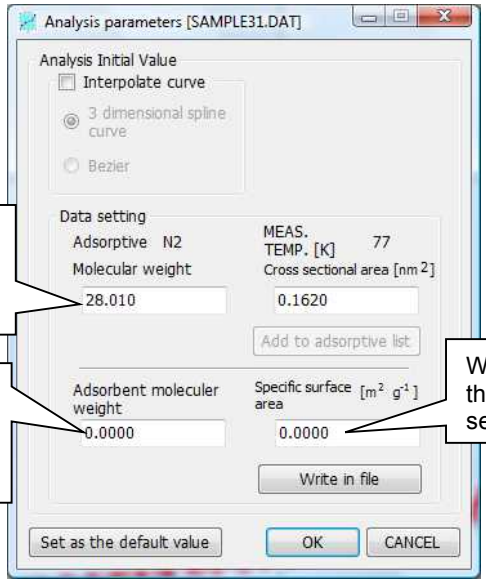
1. On the BEL analysis software menu, select “adsorption/desorption isotherm”. The program will display the following adsorption/desorption isotherm. For details about how to read the data, see “Chapter 6: Reading analysis data”, on page 30.

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:

$$y(i) = p(i) / 100$$

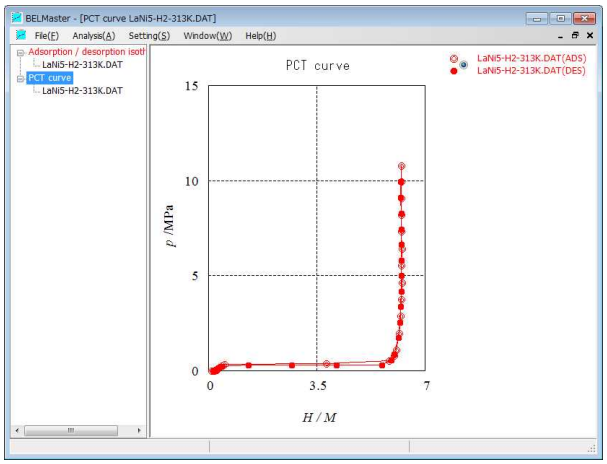
*1: Amount (mol) of hydrogen occluded by 1 mol of sample (metal).

*2: Amount (%) of hydrogen occluded by 1 g of sample (metal).

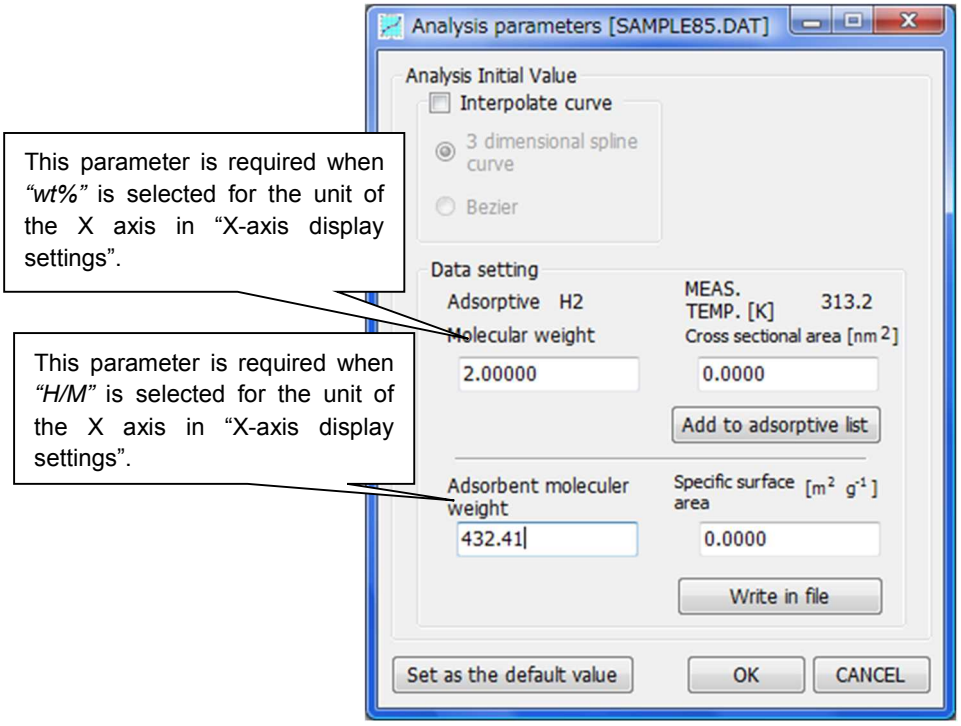
*3: Volume of gas at 0 °C and 101.325 kPa, converted from amount of adsorption by 1 g of sample (metal).

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

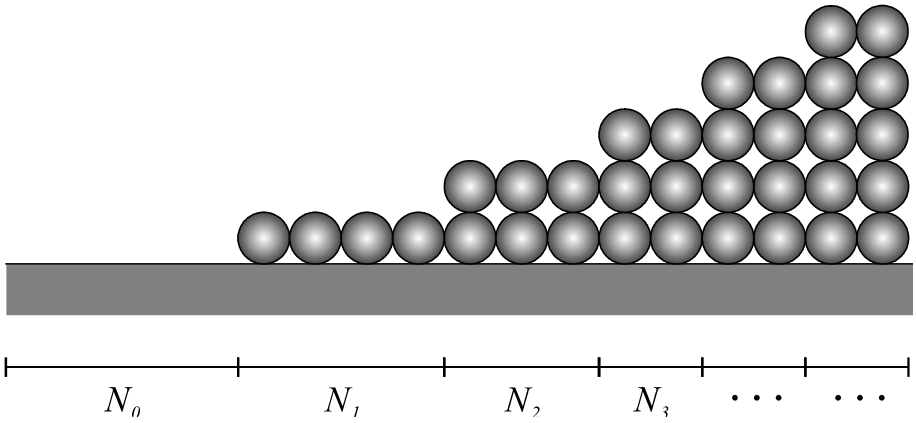
13-1-1. BET Theory

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.

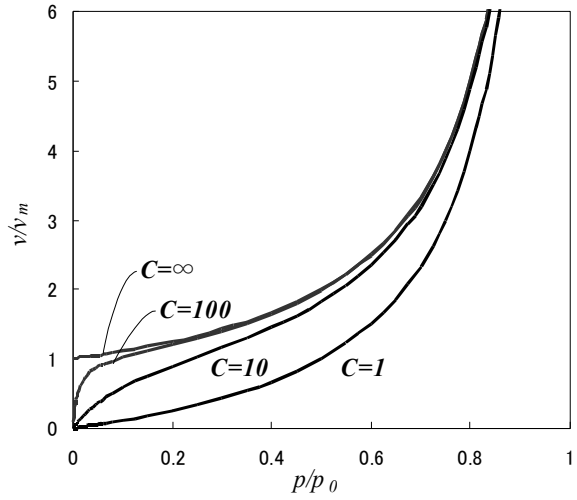
$$x = \frac{p}{p_0} \tag{13.24}$$

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»

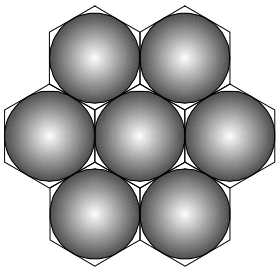
- “Adsorption of Gases in Multimolecular Layers”, Stephen Brunauer, P. H. Emmett and Edward Teller, *J. Amer. Chem. Soc.,* 60, 309(1938).
- ISO9277

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

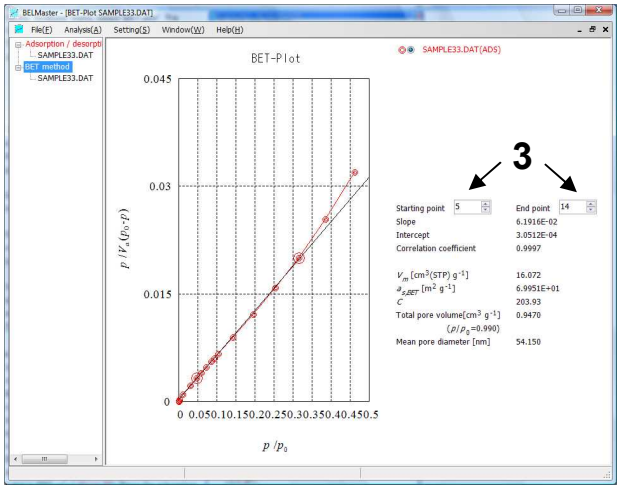
It is well-known that the gas adsorption process is essentially exothermic. The thermodynamic relation of the gas adsorption is given by equation (13.36).

$$\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad} \qquad (13.38)$$

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.

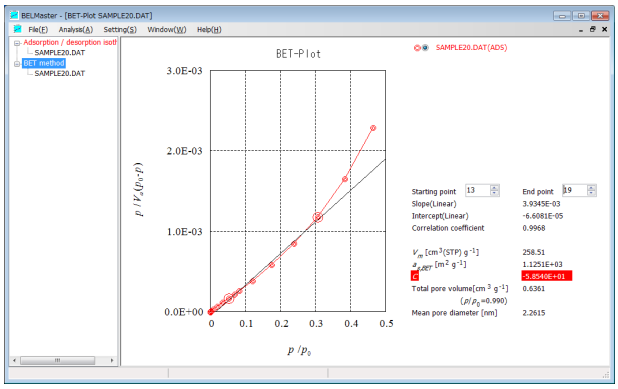


2. The program automatically draws an straight line. As a default, two points are selected that are nearest to the pressure range specified on the “Analysis parameters”.

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.

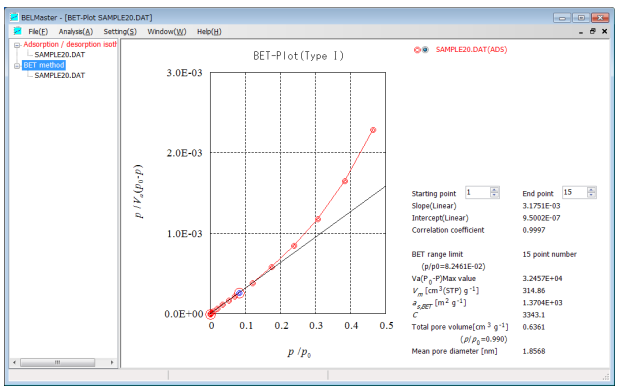
4. The figure on the right is a BET plot of nitrogen adsorption measurements on silica with micropores. The monomolecular adsorption volume (V_m/cm^3 g^{-1}) and C value can be obtained from the slope of the approximate curve and intercept. In addition, the correlation coefficient of this approximate 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)

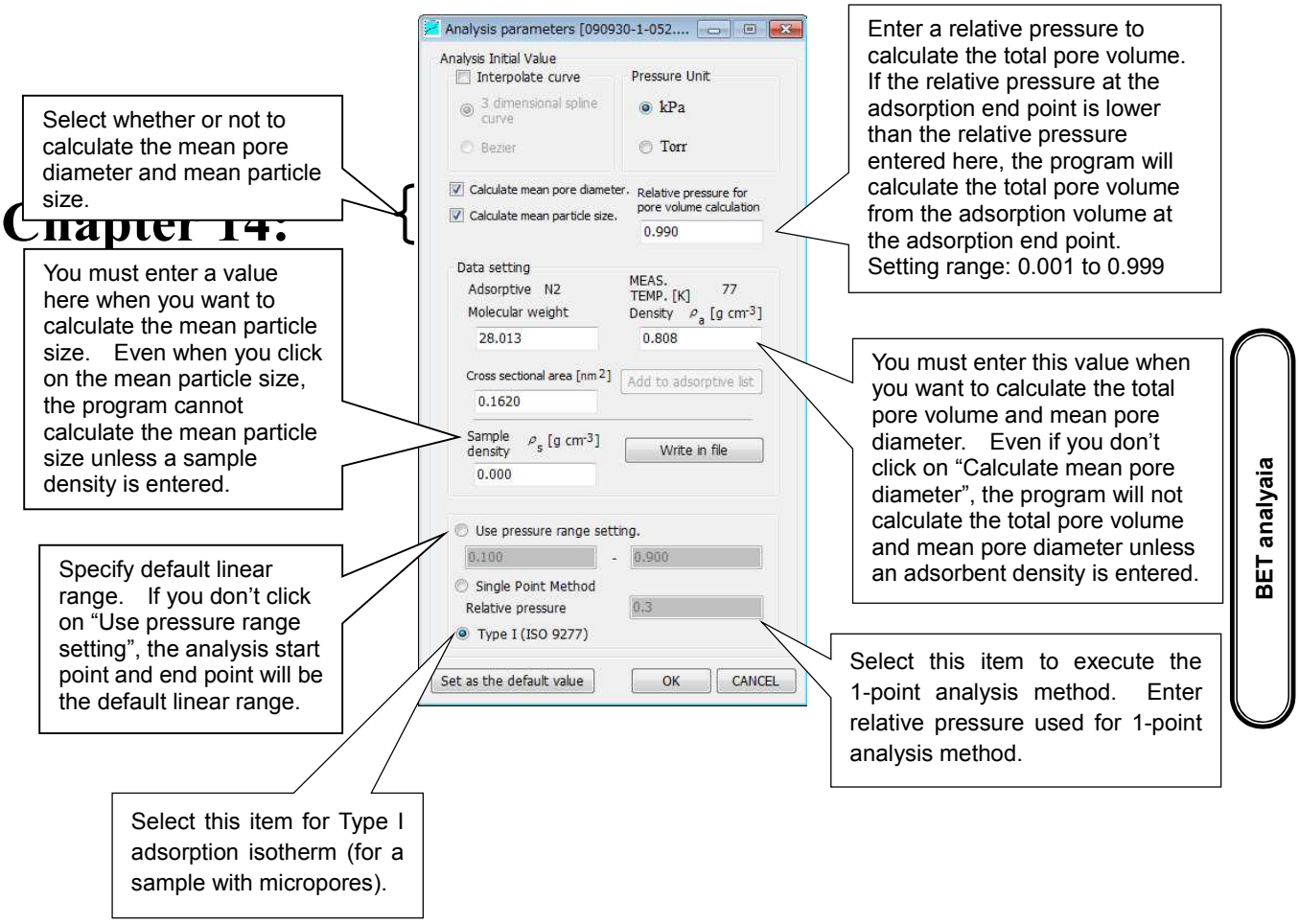
6. The figure on the right is a BET plot for activated carbon.
Regarding nitrogen adsorption on a sample with micropores, C is a negative value (indicated in red) in a relative pressure range of 0.05 to 0.03, which cannot provide a BET-plot with excellent linearity.
In this case, an accurate specific 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.

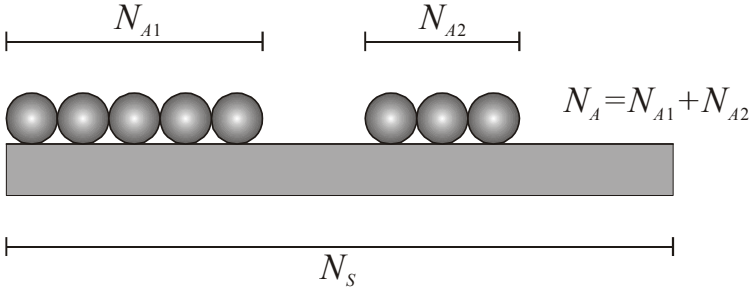


Chapter 14: Langmuir plot

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]:

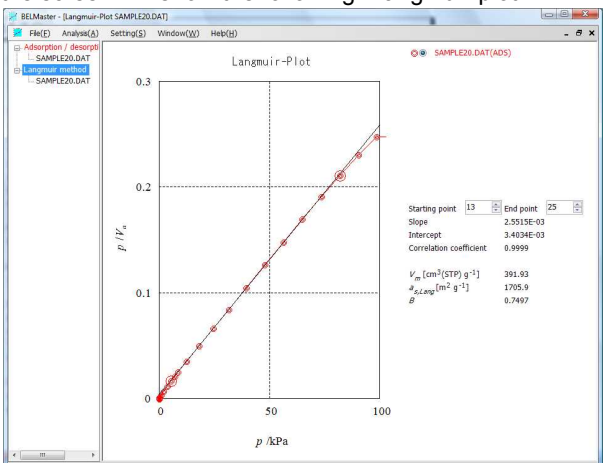
The Langmuir equation (14.7), which is derived from the adsorption model on the nonporous surface (cf. adsorption model given above), gives the Type I isotherm. In the physical adsorption, however, the Type I isotherm is obtained for the microporous adsorbents such as active carbons or zeolites. In such 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.



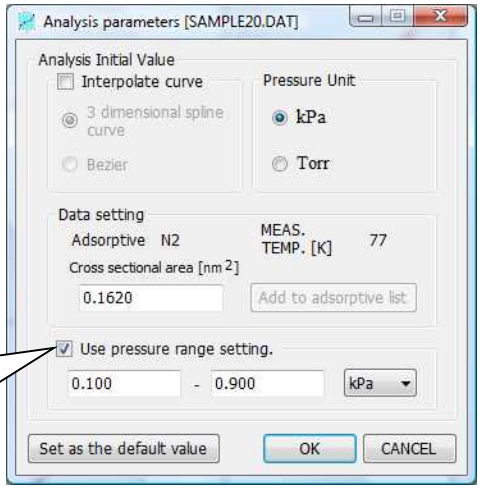
2. The program automatically draws an straight line. The default selection is the start point as the minimum data point and the end point as the maximum data point. The program obtains the monolayer volume (V_m/c m^3 g^{-1}) and the B value from the slope of the approximate curve and intercept. The program 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.

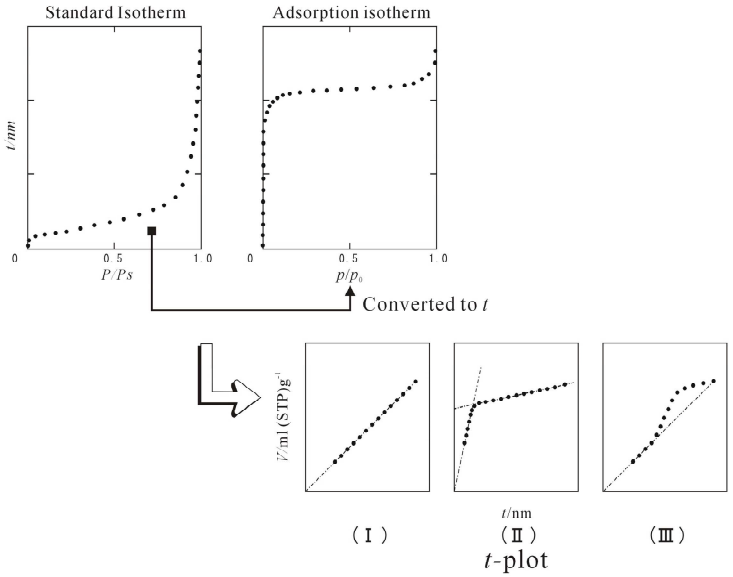
Chapter 15: t plot

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.)

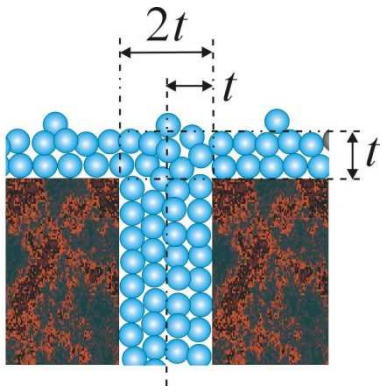
If t-plot is a linear curve that passes the original point like (I), it means that adsorption amount increased at the same rate as standard isotherm, and thus the adsorbent is considered to be non-porous material. Here, the increased adsorption amount when adsorption layer increases by one layer (*t*=0.354nm) 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.

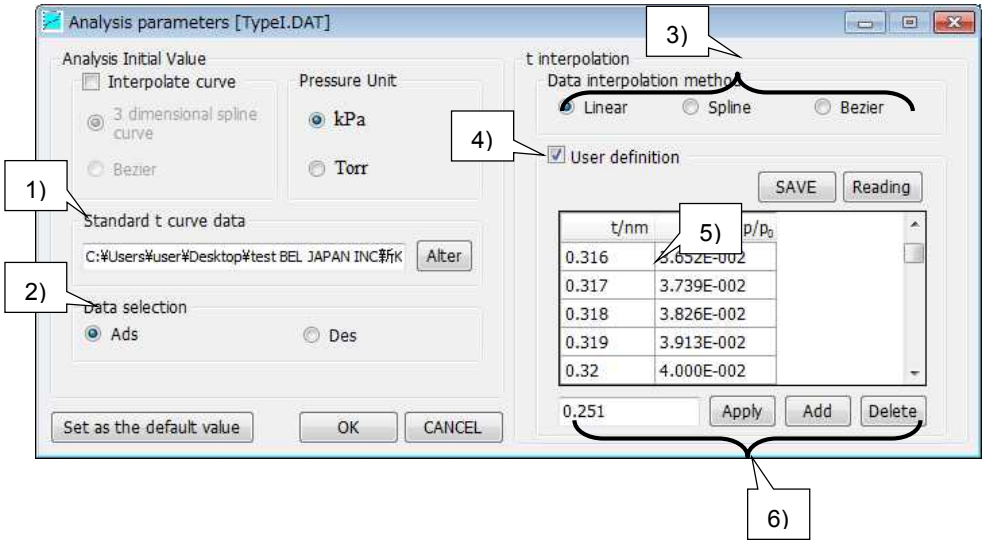
«Reference»

- "Studies on Pore Systems in Catalysts V. The *t* Method", B. C. Lippens and J. H. de Boer, *J. Catalysis,* 4, 319 (1965).

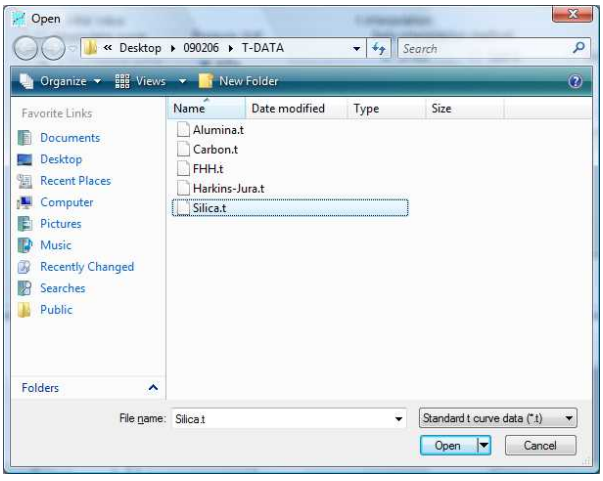
15-2. Operation

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].

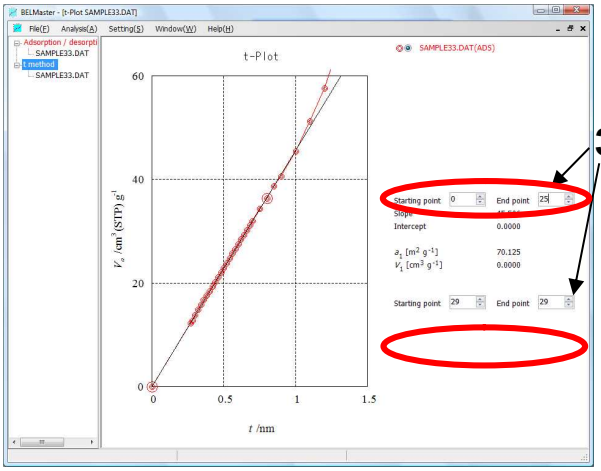


2) Select which data will be used for calculation, the adsorption branch or desorption branch.
3) Select an interpolation method for the file data.
   - You can set the interpolation method to Linear, Spline or Bezier.
4) If interpolation method is not selected, the program will calculate a t-plot at 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.

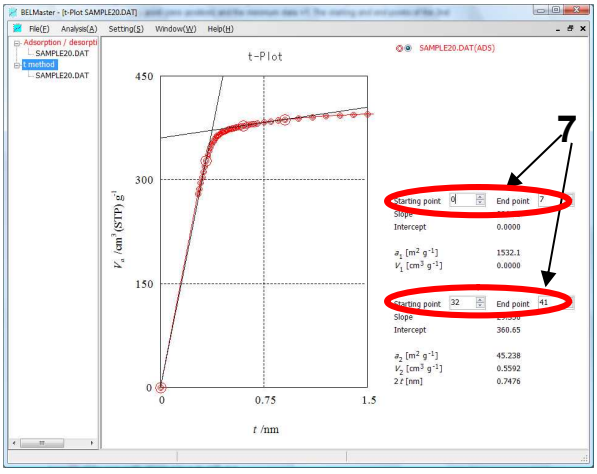
3. In a t-plot, the program will automatically draw two straight lines. The default starting and end points of the 1st line are the minimum data point (zero position) and the minimum data +1. The starting and end points of the 2nd line are the maximum data point -1 and the maximum data point.

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.

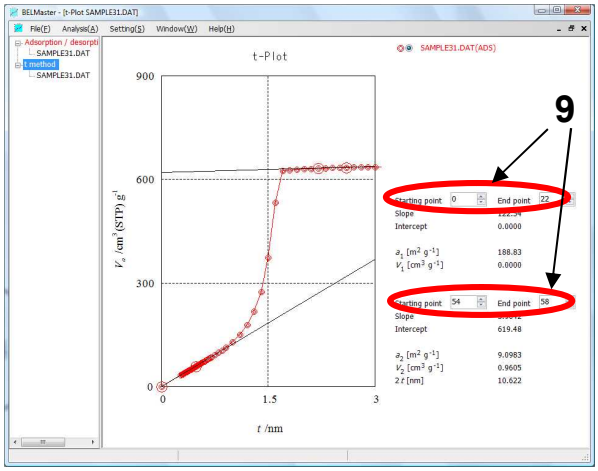


7. Select a starting point (normally the zero position) and end point of the first straight line. The program will calculate the specific surface area (a_1) 1,532 m^2 g^{-1} from the slope of this straight line. Select the starting and end points of the 2nd line. Using the slope of this straight line, 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.

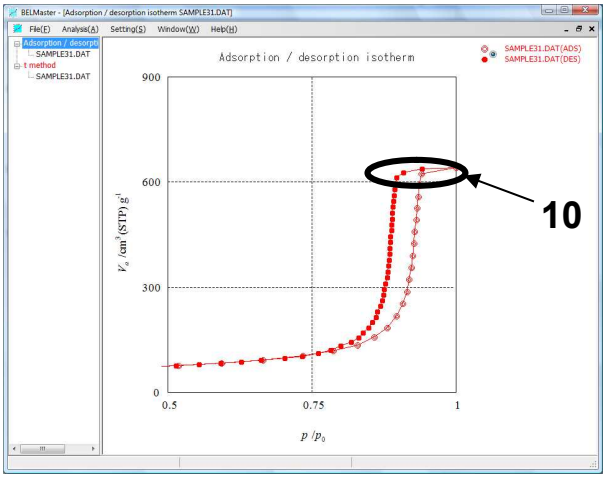
8. The figure on the right is a t-plot of a nitrogen isotherm for mesoporous silica. “silica-BET.t” is used as a standard isotherm. The “User definition” was clicked on and the calculation range was widened to 3 nm.



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)]

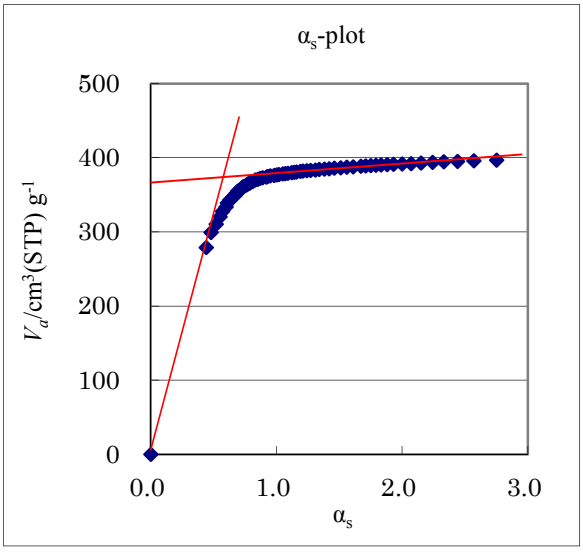
$$\alpha_s = \frac{n_a}{n_{0.4}} \qquad (16.2)$$

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.

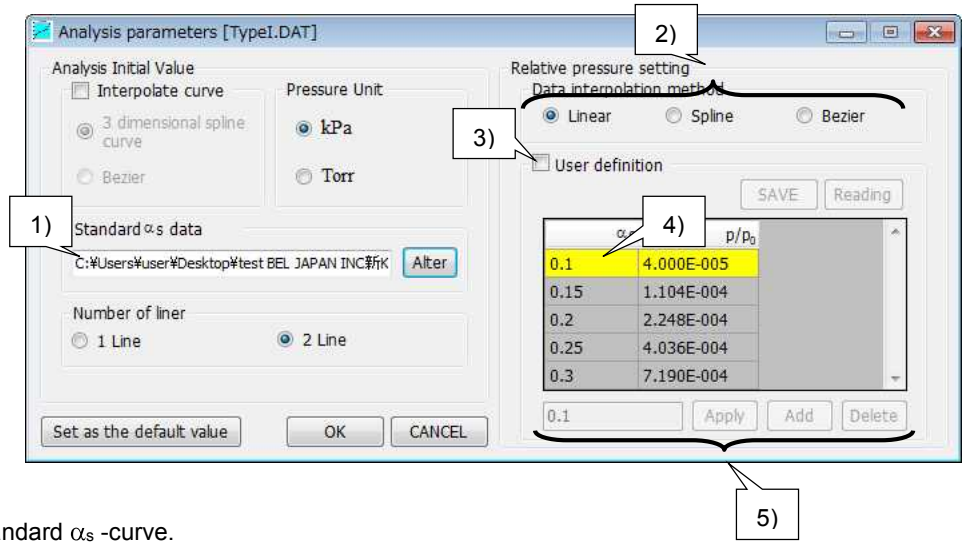
«Reference»

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)

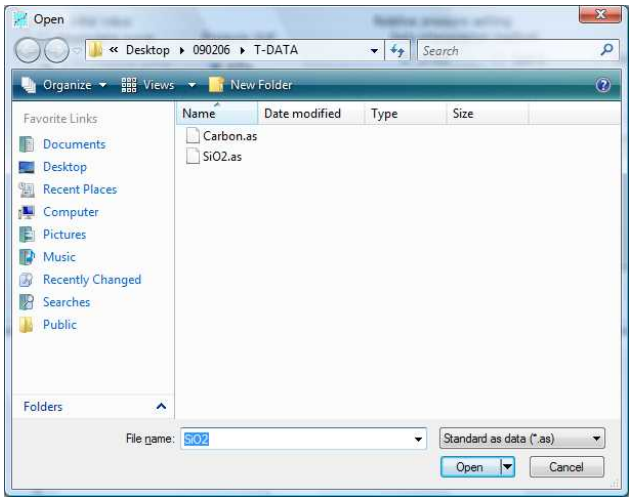
16-2. Operation

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.

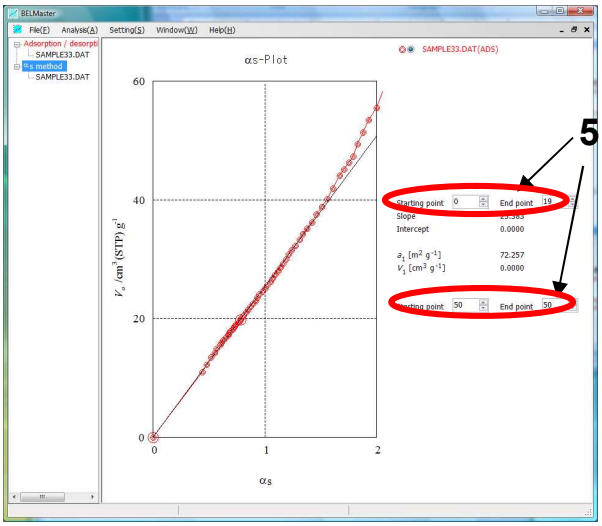


2) Select a method for interpolating the file data.
   - You can select Linear, Spline or Bezier.
3) If “User defintion” is not clicked, the program will calculate an αs -plot at the default setting point. When you click on “User definition”, the program will calculate the αs value specified in the table 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.

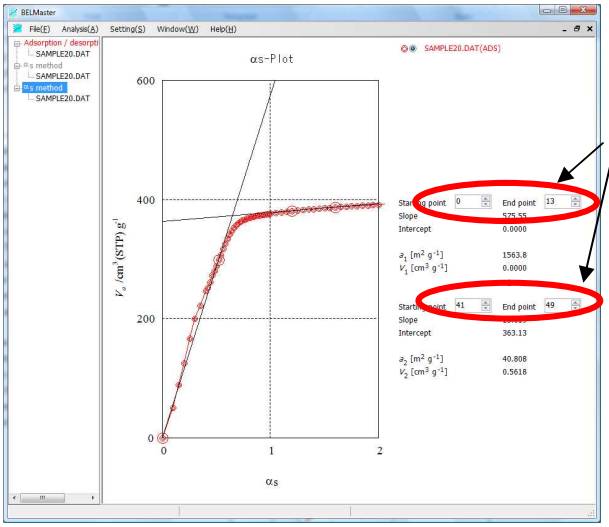
- Click on the [Add] button. The data displayed in the box will be added.
- The modified and added data are sorted automatically in top to bottom order.
- Click on the [Delete] button and the selected data will be deleted.

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.



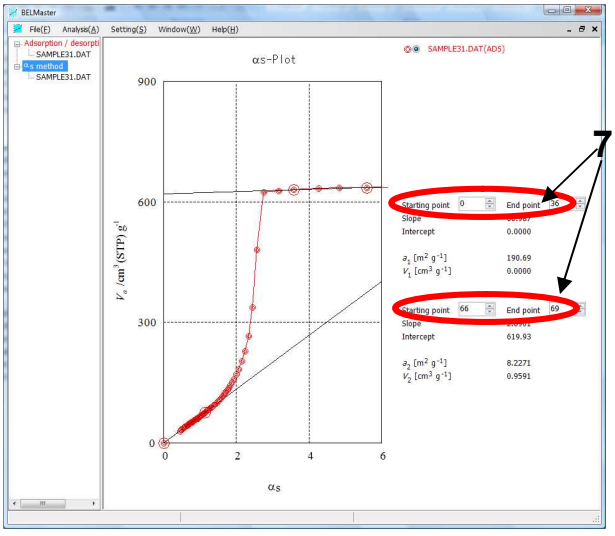
4. The figure on the right is an α_s -plot of a nitrogen adsorption isotherm for macroporous silica. “SiO2.as” is used as a standard isotherm. When selecting a standard isotherm whose chemical characteristics are similar to the sample surface, good linearity can be obtained as the α_s -plot passes through 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).

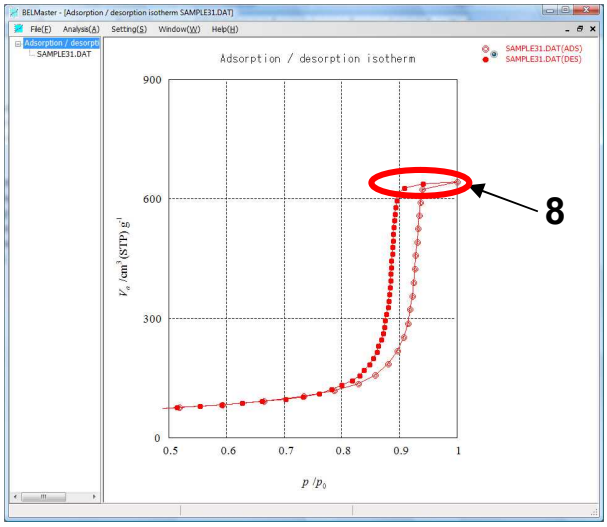
7. The figure on the right is an α_s -plot of nitrogen adsorption isotherm for mesoporous silica. “silica-BEL.as” is used as a standard isotherm. Select a starting point (normally the zero position) and an end point for the 1st straight line. The program will calculate the specific area (a_1) 191 m^2 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

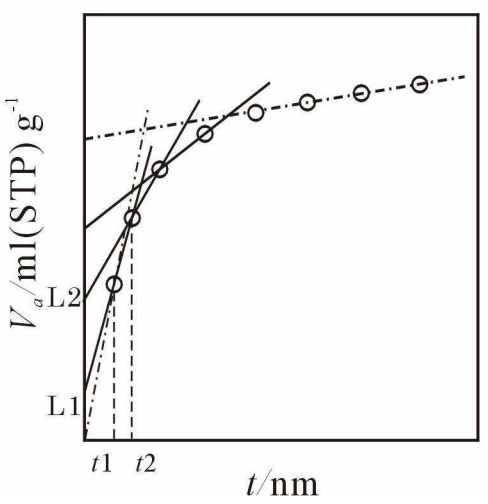
Chapter 17: MP method analysis

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.

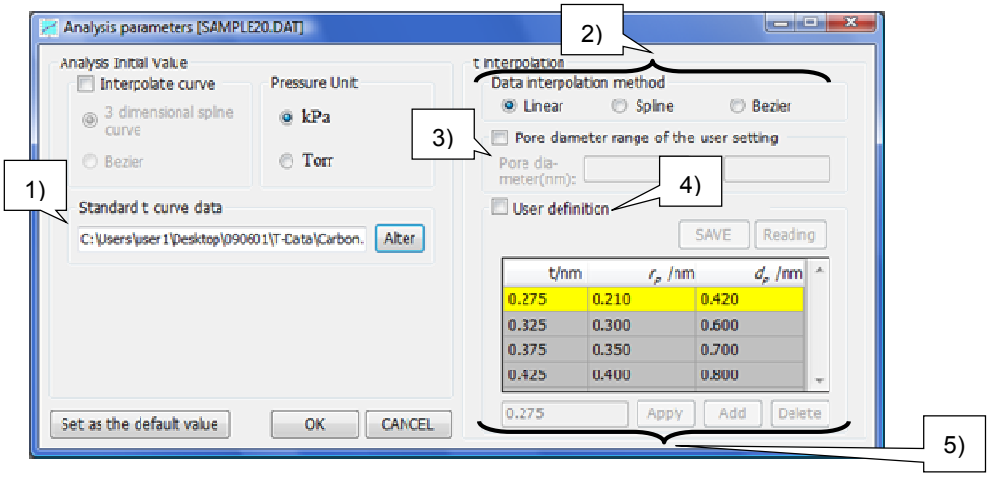
«Reference»

- "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).

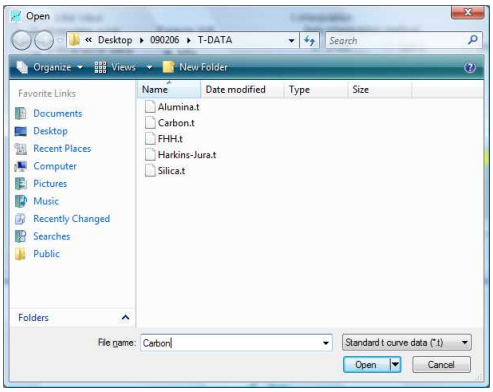
17-2. Operation

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.

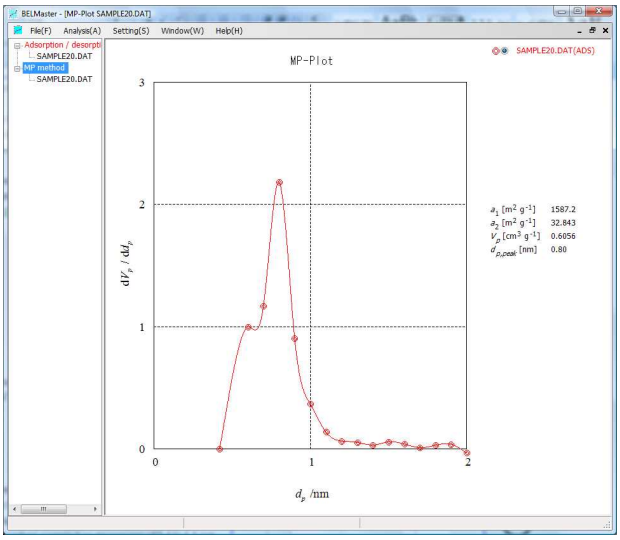


1) Select a standard t-curve.
   - Select a standard isotherm that has similar chemical characteristics to the sample surface.
   - Click on the [Alter] button and the following selection window will appear. Select a standard t-curve data file and click on the [Open] button.

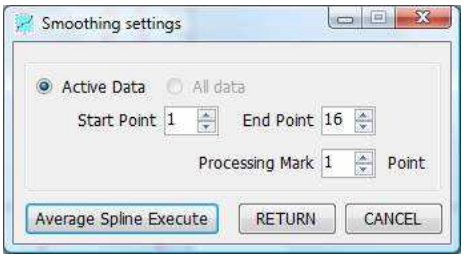


2) Select an interpolation method for the file data.
   - You can select Linear, Spline or Bezier.
3) If “Pore diameter range of the user setting” is not selected, the program will calculate using the default range. When “Pore diameter range of the user setting” is selected, the program will calculate 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.

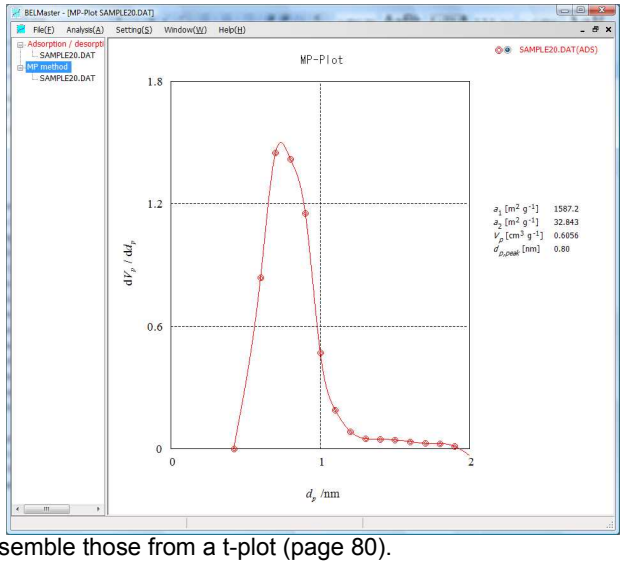
- Click on the [Add] button and the data displayed in the box will be added.
- The modified and added data are automatically sorted in order from top to bottom.
- Click on the [Delete] button and the selected data will be deleted.



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.



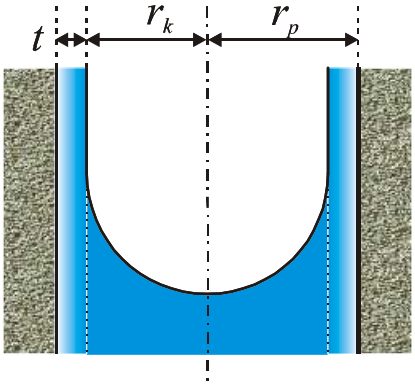
5. The figure on the right shows the result of clicking on the [Average Spline Execute] button to perform one round of smoothing. It can be seen from the figure that this activated carbon sample has micropores of 0.4 to 1.1 nm diameter (d_p), and has a distribution peak ($d_{p,peak}$/nm) at 0.8 nm. From 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.

$$r_p = t + r_k \tag{18.1}$$

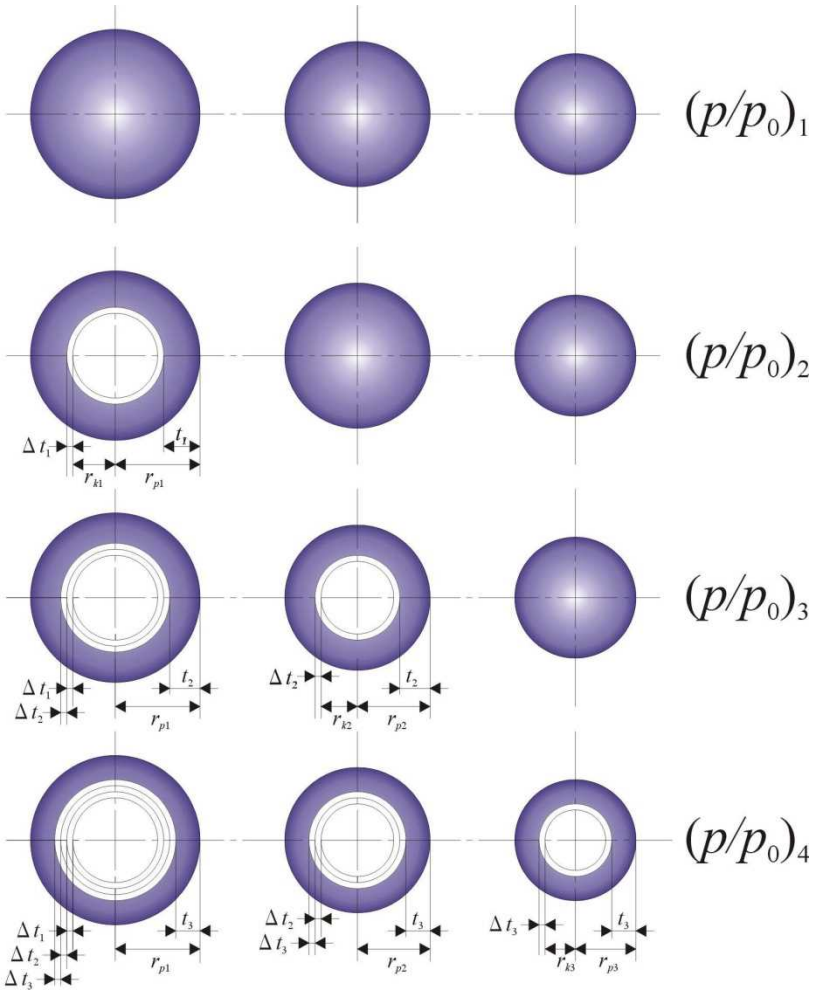
Thickness of adsorption layer can be calculated from *t* curve of standard sample, and core radius can be calculated by Kelvin equation (18.2).

$$\ln\frac{p}{p_0} = -\frac{2\gamma V_L}{RT}\frac{1}{r_m} \tag{18.2}$$

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:

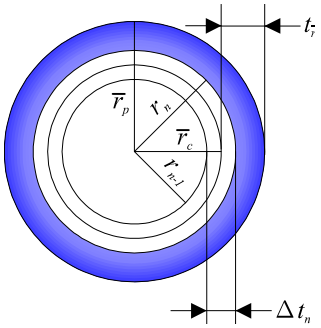
$$V_{\Delta t2} = \Delta t_2 \times Ac_1 \tag{18.9}$$

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.

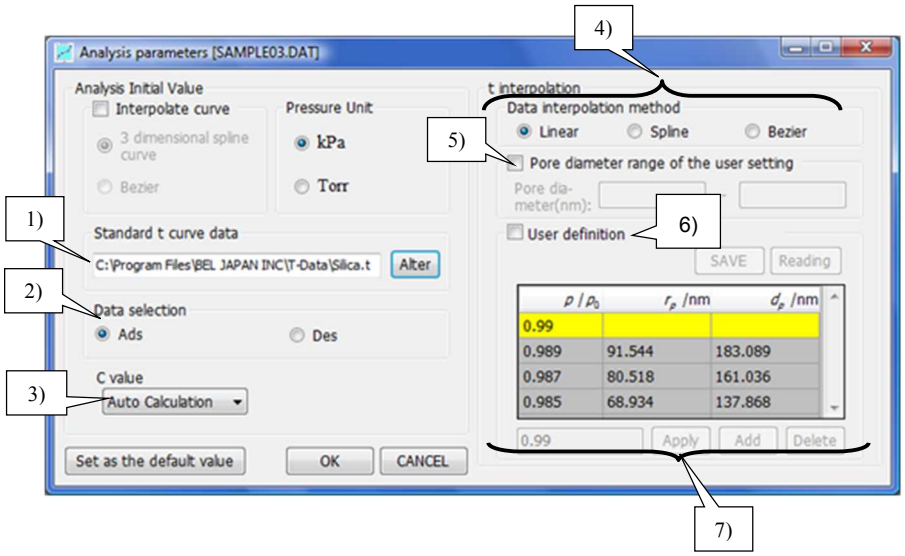
«Reference»

- "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).

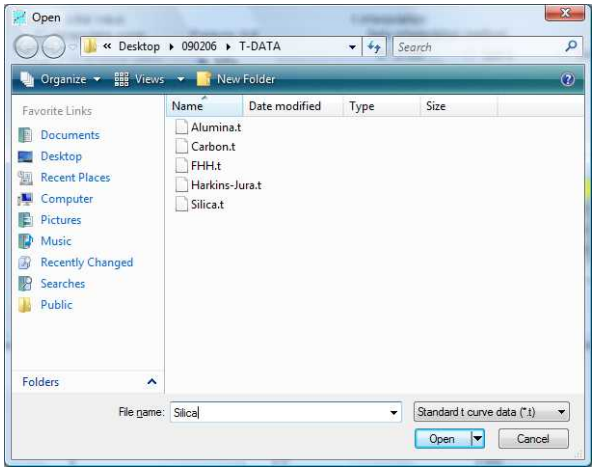
18-2. Operation

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.



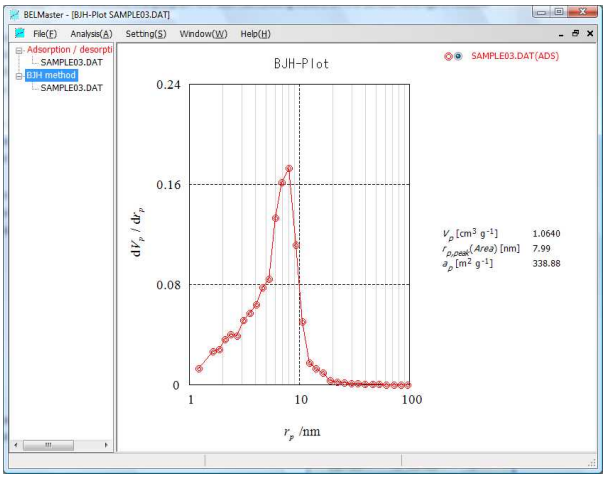
1) Select a standard t-curve.
   - Select a standard isotherm that has similar chemical characteristics to the sample surface.
   - Click on the [Alter] button and the following selection window will appear. Select a standard t-curve data file and click on the [Open] button.



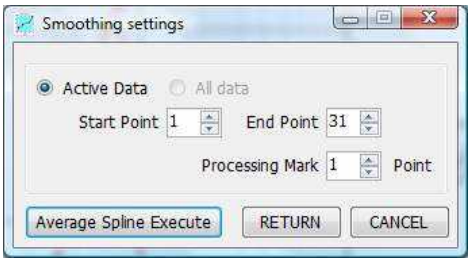
2) Select which data will be used for calculation, the adsorption branch or desorption branch.
   - Most porous samples have a pore size distribution. It is believed that distribution of pore size in these samples can be obtained from the adsorption process, and the distribution of the bottle neck can 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.

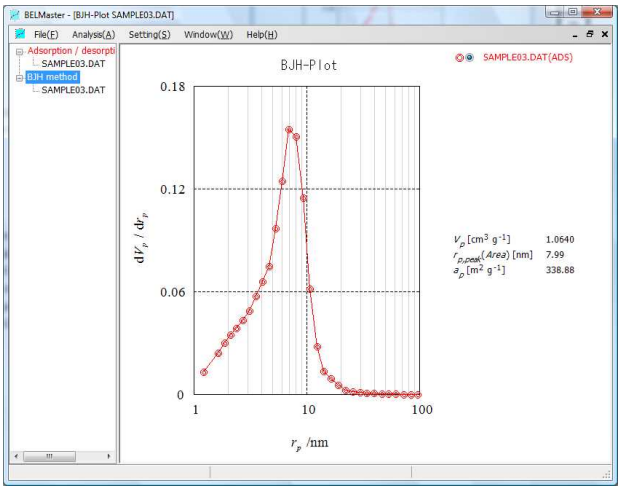
3. The figure on the right is a BJH-plot (differential curve) of a nitrogen adsorption isotherm for mesoporous silica. “silica-BEL.t” is used as a standard isotherm.



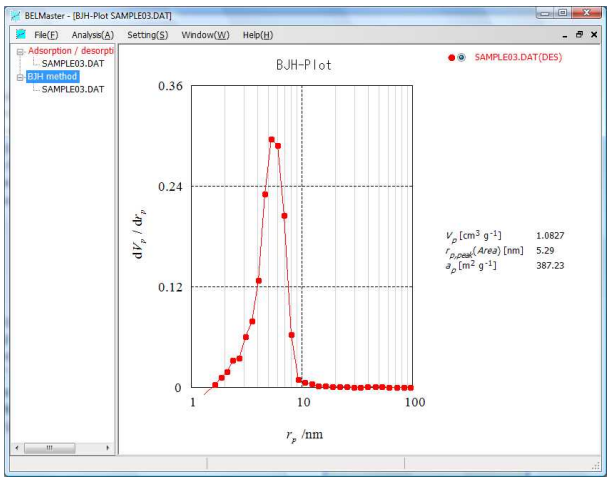
4. When you want to smooth the data, select “Smoothing settings” on the “Setting” menu. The “Smoothing settings” window shown on the right will appear.



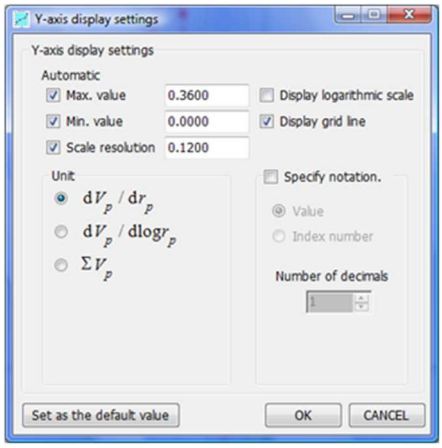
5. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 2 to 15 nm radius, and it has a distribution peak at 8.0 nm. The integrated pore volume (V_p) will be 1.064 cm^3 g^{-1}.



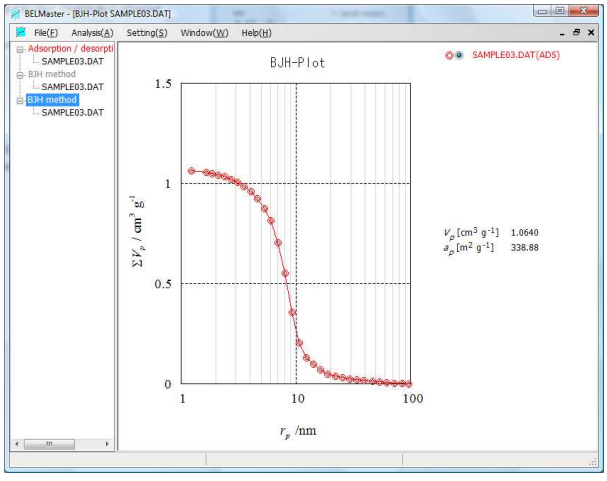
6. For this silica, select the desorption process on the "Analysis parameters" window. The figure on the right shows a result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 3 to 9 nm radius at 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.

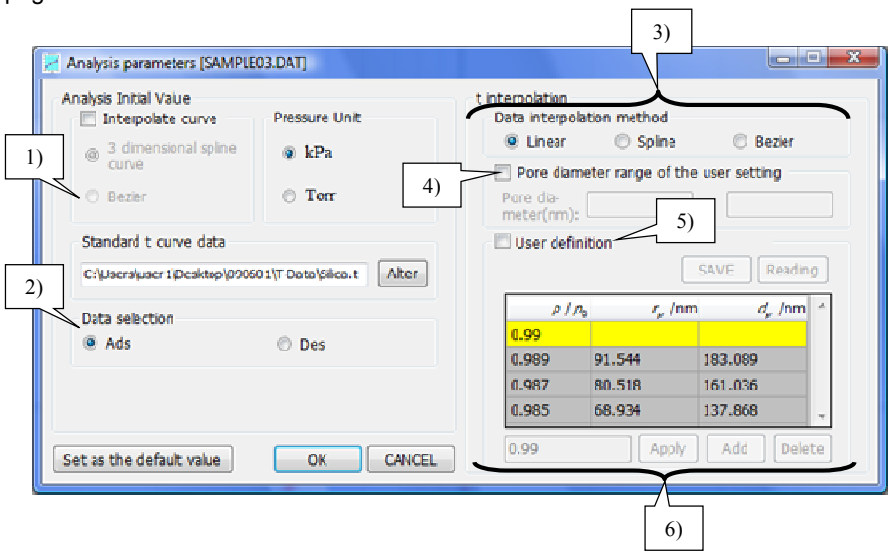
«Reference»

- "The Determination of Pore Structures from Nitrogen Adsorption Isotherms", R. W. Cranston and F. A. Inkley, *Advan. Catalysis,* 9, 143 (1957).

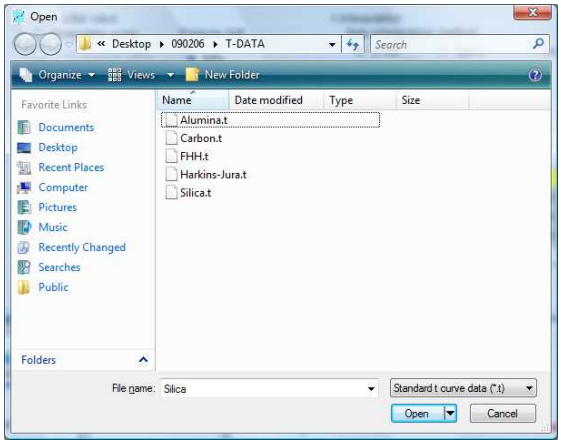
19-2. Operation

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

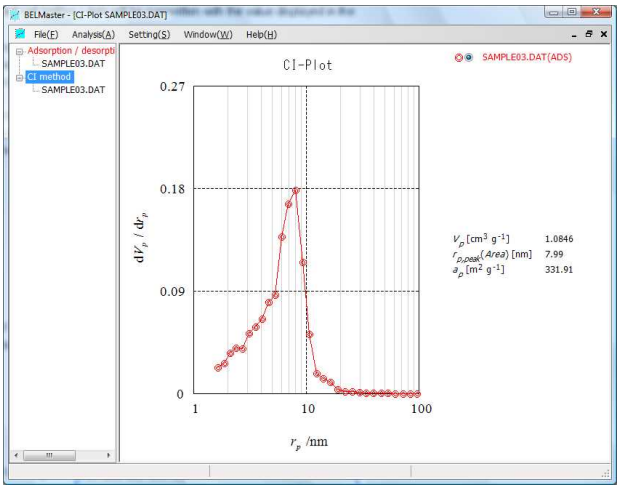
specified in the table below.

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.

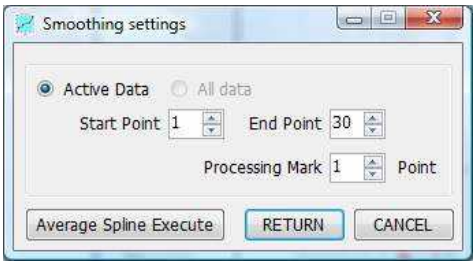
6) Relative pressure settings.

- 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.

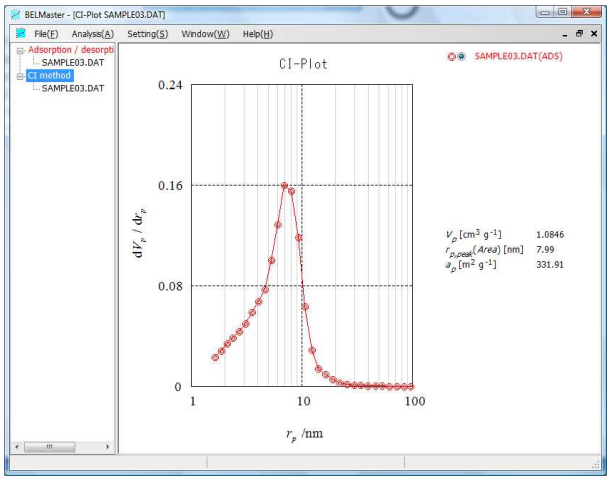
3. The figure on the right is a CI-plot (differential curve) of a nitrogen adsorption isotherm for mesoporous silica. “silica-BEL.t” is used as a standard isotherm.



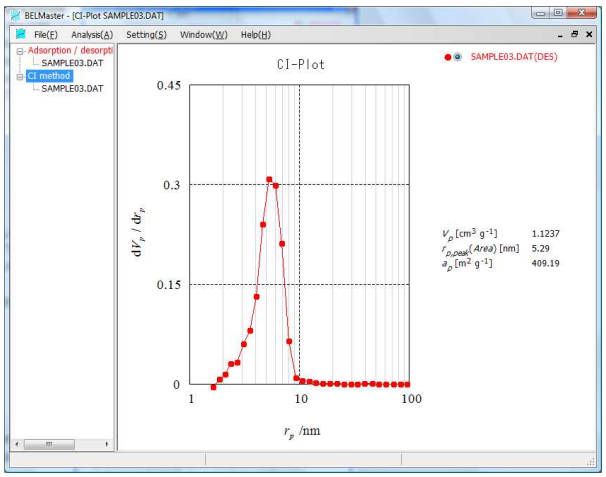
4. When you want to smooth the data, select “Smoothing settings” on the “Settings” menu. The “Smoothing settings” window shown on the right will appear.



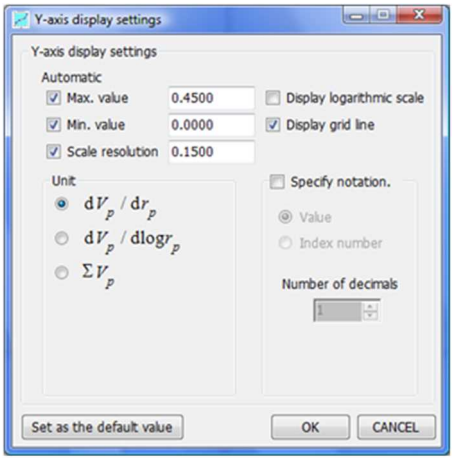
5. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 2 to 15 nm radius, and has a distribution peak at 8.0 nm. The integrated pore volume (V_p) will be 1.085 cm^3 g^{-1} and the integrated pore area (a_p) is 332 m^2 g^{-1}.



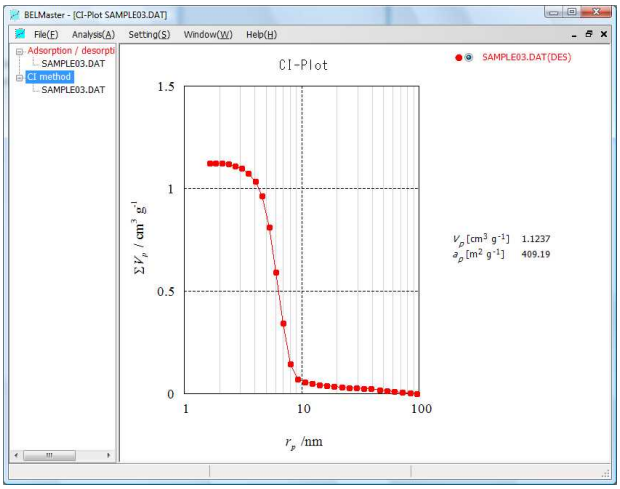
6. Select the desorption process to use for this silica sample on the “CI-plot setting” window. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 3 to 9 nm 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).

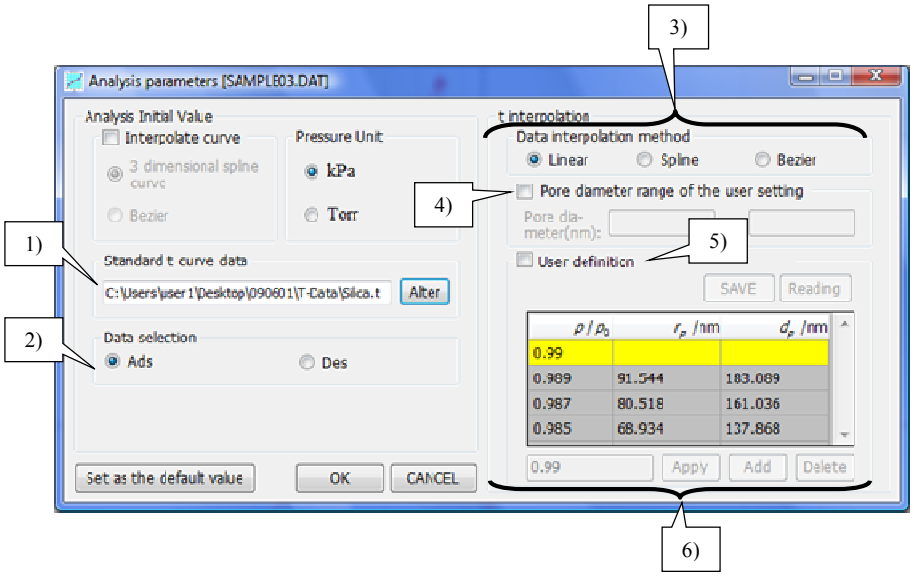
«Reference»

- D. Dollimore and G. R. Heal, *J. Applied Chem.* 14, 109 (1964); *J. Colloid Interfasce Sci.* 33, 508 (1970).

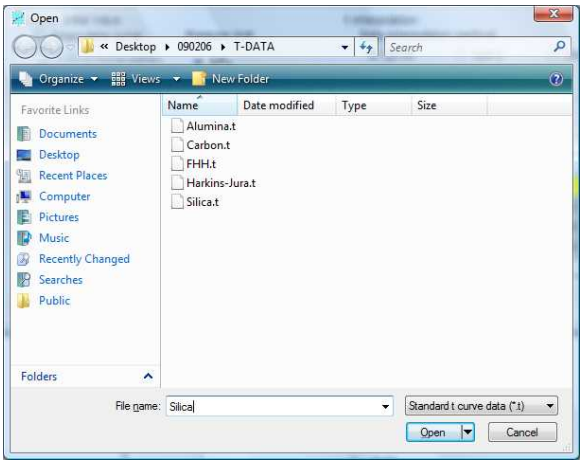
20-2. Operation

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.

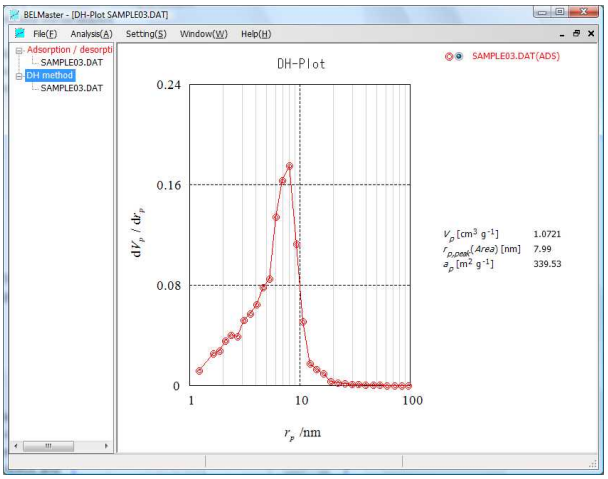
4) If “Pore diameter range of the user setting” is not selected, the program will calculate using the default range. When “Pore diameter range of the user setting” is selected, the program will calculate the pore diameter range specified in the table below.

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.

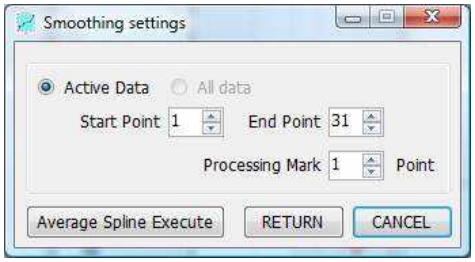
6) Relative pressure settings.

- 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.

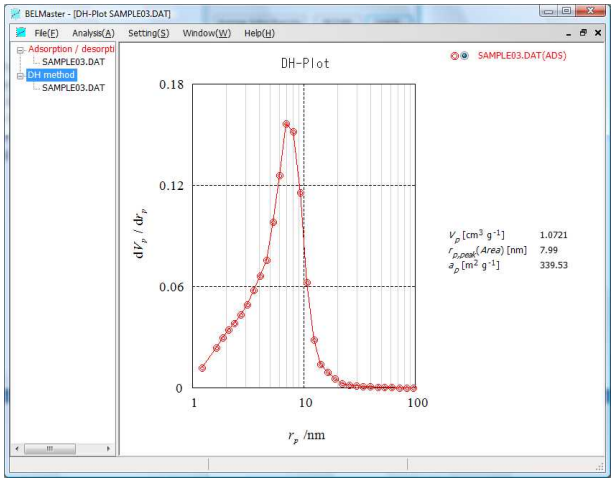
3. The figure on the right is a DH-plot (differential curve) of a nitrogen adsorption measurement on mesoporous silica. “silica-BEL.t” is used as a standard isotherm.



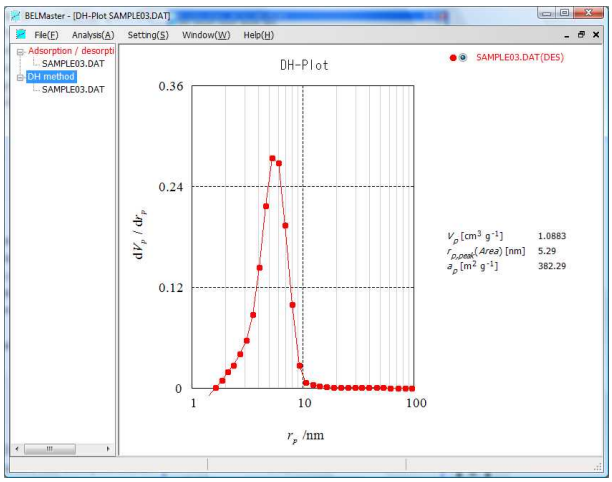
4. When you want to smooth the data, select “Smoothing settings” on the “Settings” menu. The “Smoothing settings” window shown on the right will appear.



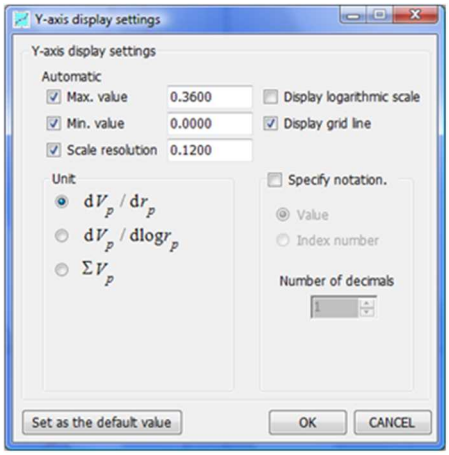
5. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 2 to 15 nm radius, and has a distribution peak at 8.0 nm. The integrated pore volume (V_p) will be 1.07 cm^3 g^{-1} and the integrated pore area (A_p) is 340 m^2 g^{-1}.



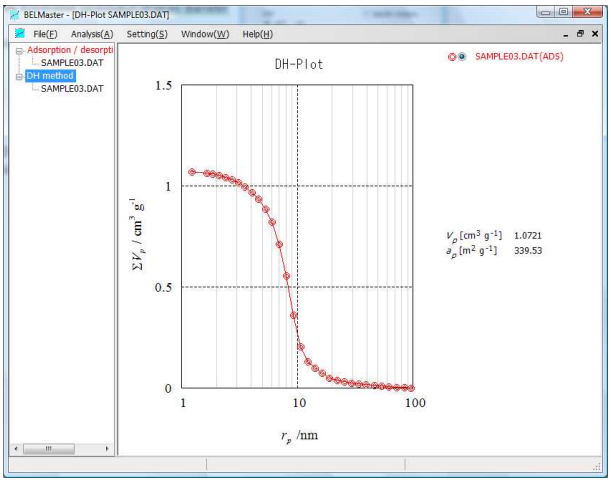
6. Select the desorption process for this silica sample in the “DH-plot setting” window. The figure on the right shows the result of clicking the [Average Spline Execute] button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores of 3 to 9 nm radius, 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.

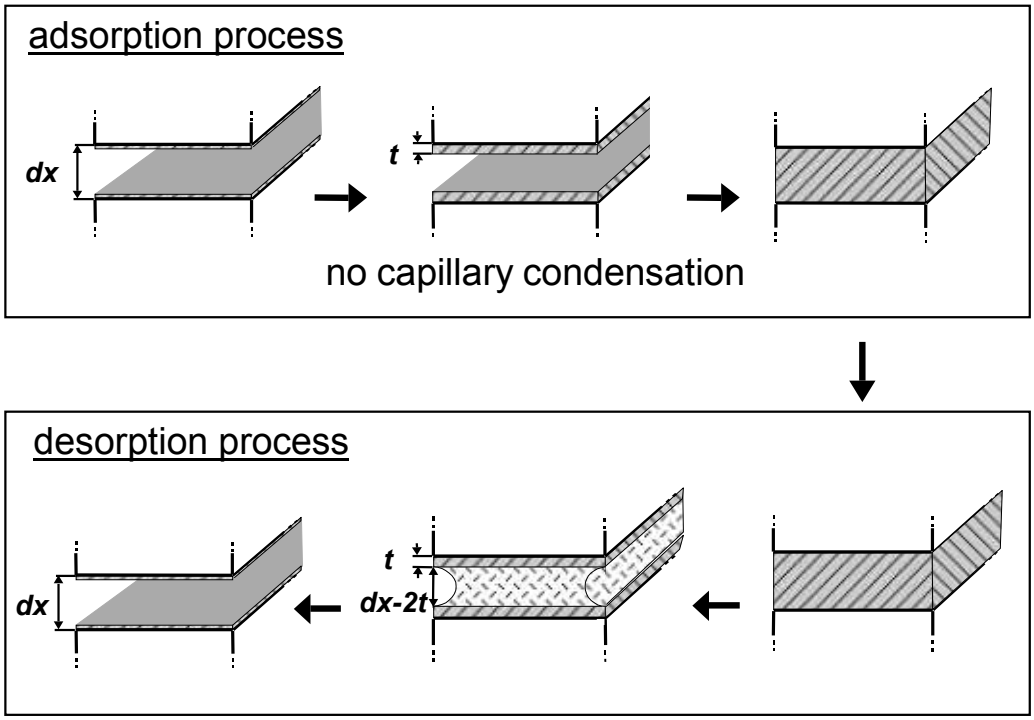


Chapter 21: INNES plot

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).

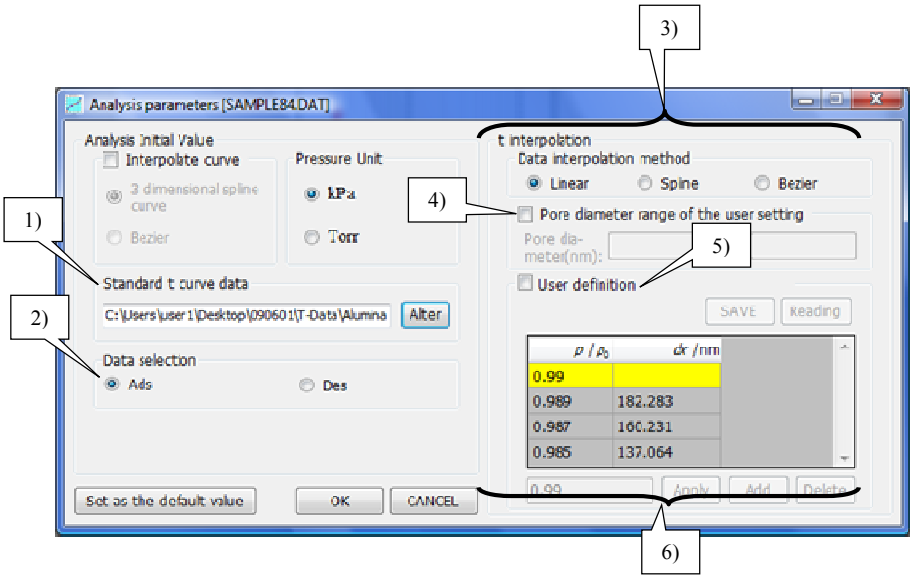
«Reference»

- F. Rouquerol, J. Rouquerol & K. Sing “Adsorption by powders & porous solids (Academic Press, 1999)”, 440
- W. B. INNES “Analytical Chemistry”, 29, 1069 (1957).

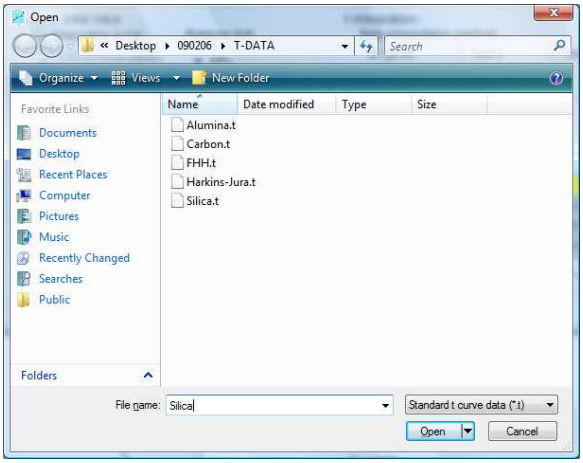
21-2. Operation

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.

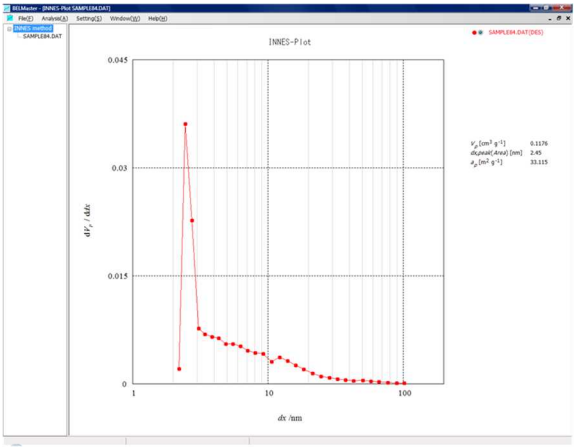
4) If “Pore diameter range of the user setting” is not selected, the program will calculate using the default range. When “Pore diameter range of the user setting” is selected, the program will calculate the pore diameter range specified in the table below.

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.

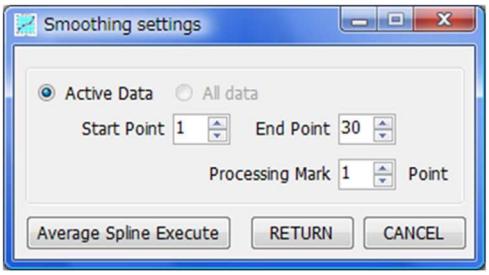
6) Relative pressure settings.

- 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.

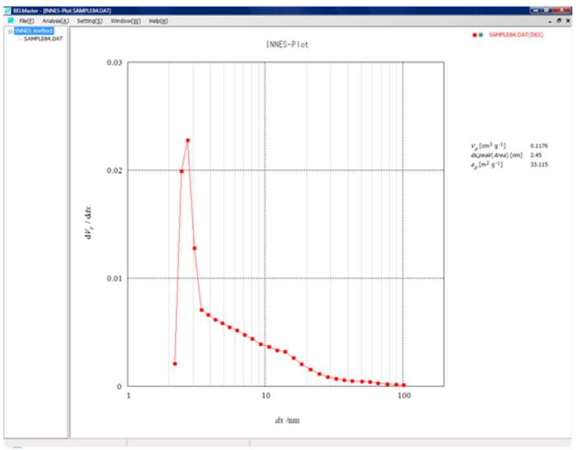
3. The figure on the right shows an INNES-plot curve (differential curve) obtained with measurement (desorption process) of nitrogen adsorption into a clay mineral with slit-shaped pores. “alumina-BEL.t” is specified as a standard isotherm.



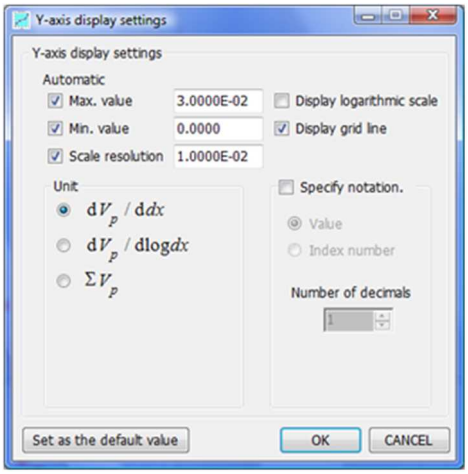
4. When you want to smooth the data, select “Smoothing settings” on the “Settings” menu. The “Smoothing settings” shown on the right will appear.



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.

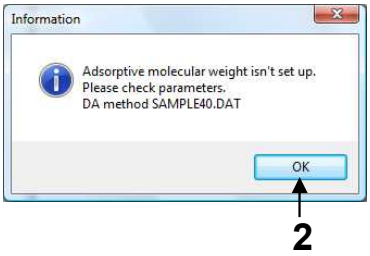
«Reference»

- "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

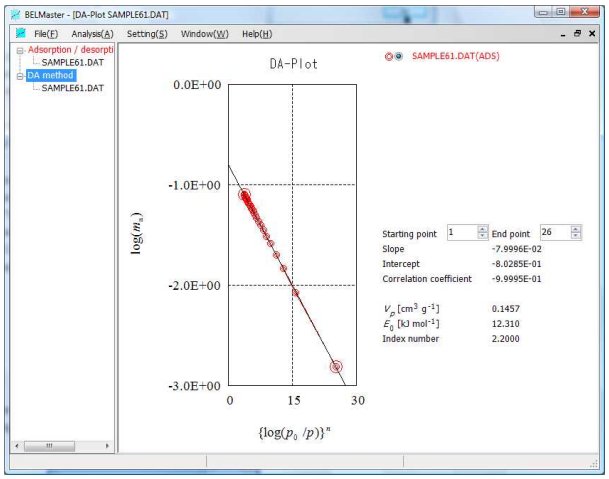
1. On the “Analysis (A)” menu, select “DA plot” and the screen will show the following DA plot windows. The program will execute a DA plot from the adsrotption data of an isotherm.

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.

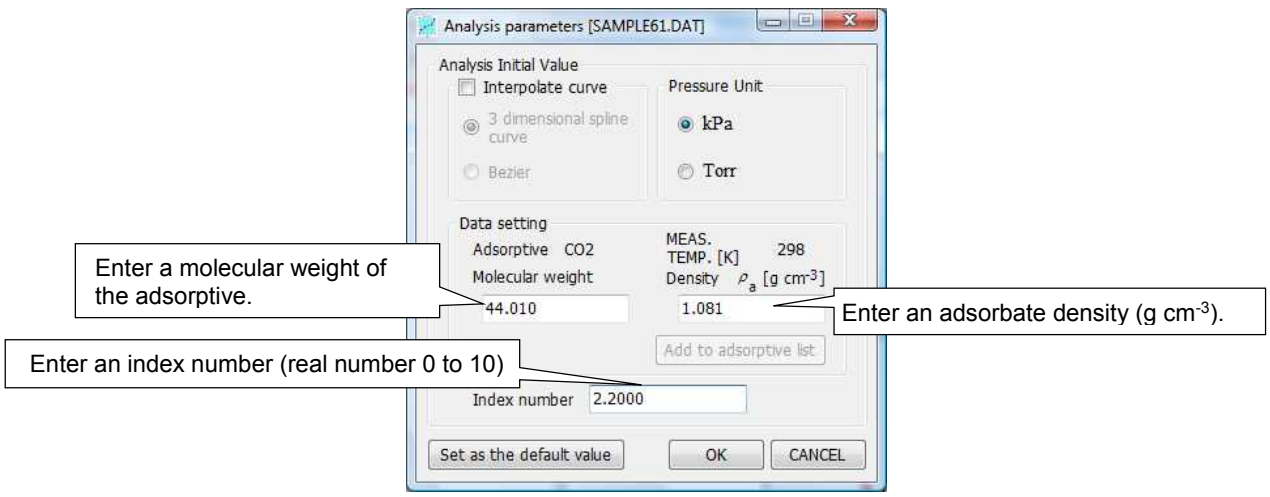
$$V = \frac{m_a}{\rho_a}$$

$$V_p = \frac{10^i}{\rho_a}$$

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.



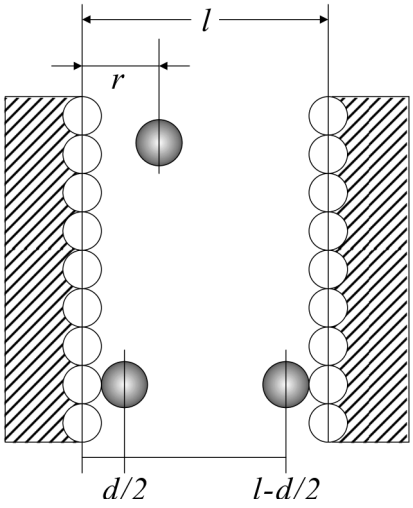
Chapter 23: HK plot

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**)

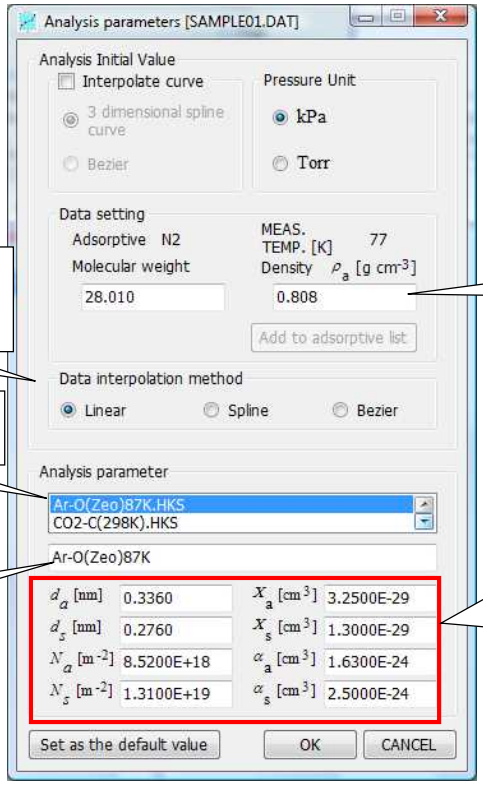
Physical quantity	Adsorbent parameters		Adsorptive parameters		
	Carbon	Zeolite	Nitrogen	Argon	Carbon dioxide
Diameter (nm)	0.34	0.28	0.30	0.34	0.40[1)]
Polarizability α (cm^3)	1.02 x 10^{-24}	2.50 x 10^{-24}	1.46 x 10^{-24}	1.63 x 10^{-24}	2.91 x 10^{-24} [2)]
Magnetic susceptibility χ (cm^3)※	13.5 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.

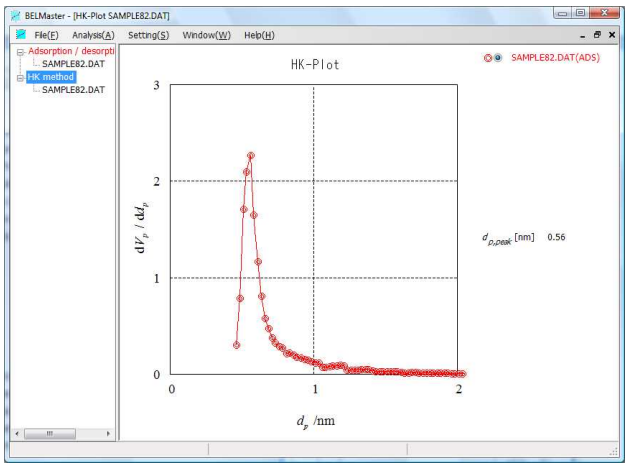
The currently selected parameter filename is displayed.

Enter a molecular weight and a density for the adsorbate.

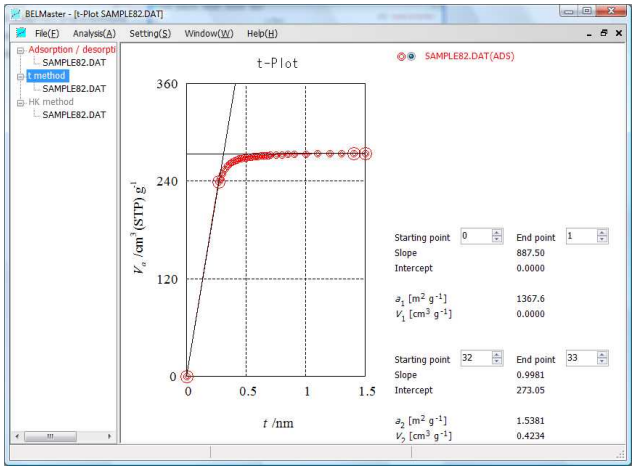
Enter parameters such as the molecular size and magnetic susceptibility. For details about each parameter, see the table below or the respective description.

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.



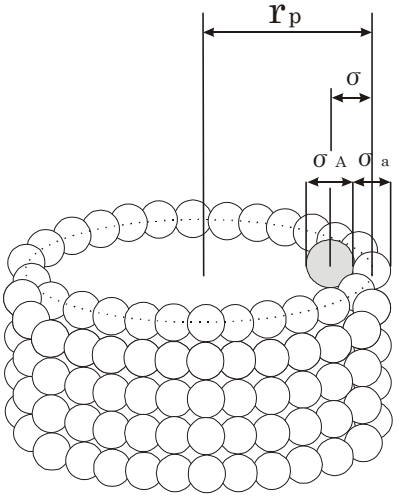
Chapter 24: SF plot

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 $AlPO_4$.

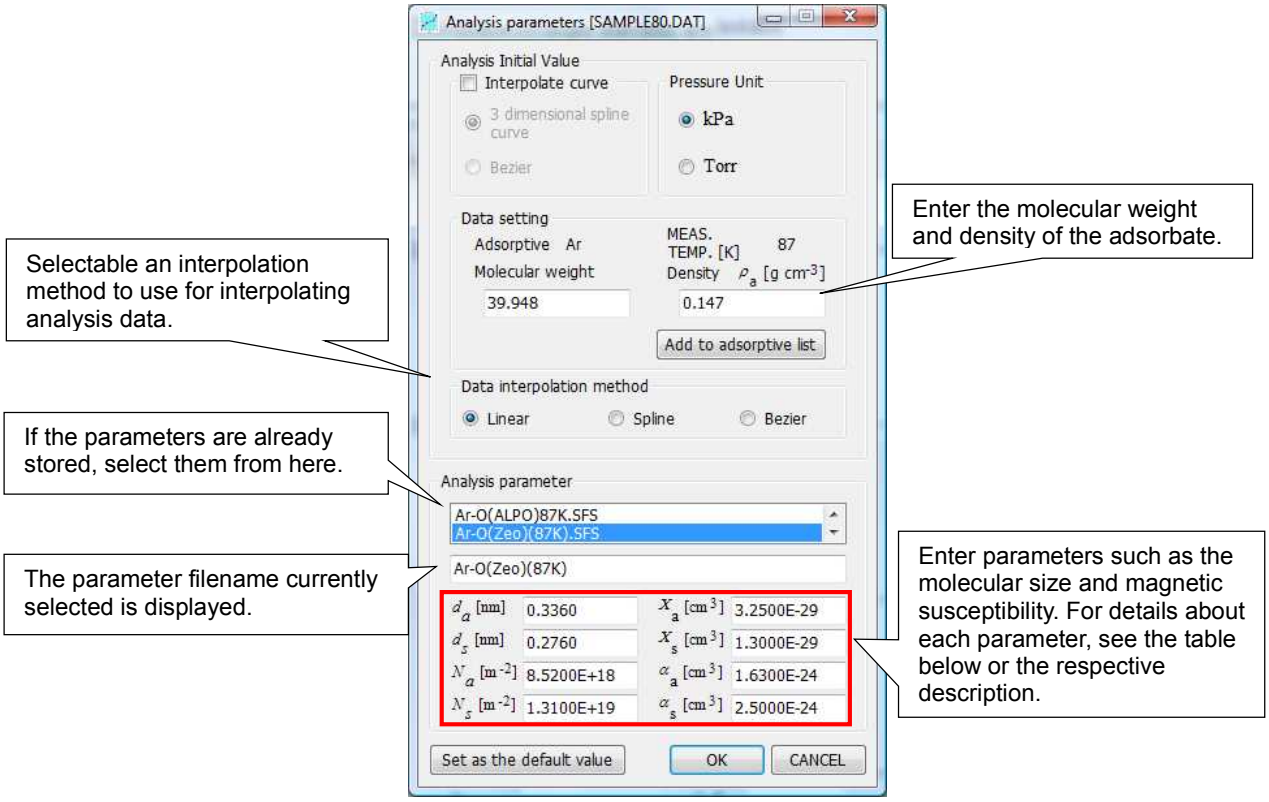
In micropore calculation, pore size is determined first, then relative pressure respect to the pore size is calculated using the equation (24.2). Integral curve can be obtained by calculating the adsorption amount against relative pressure that is obtained from (24.2) by interpolation equation using 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

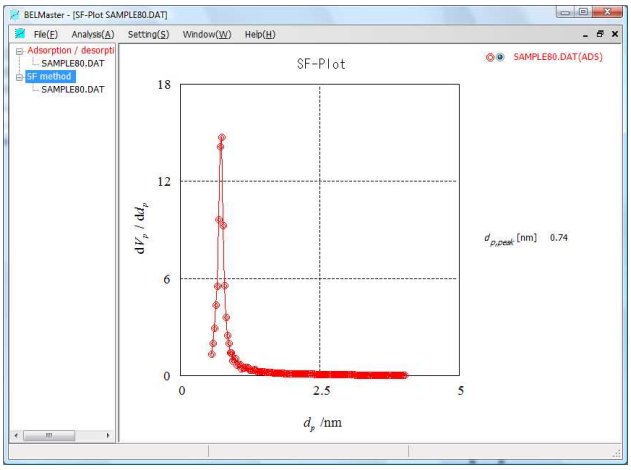
1. On the “Analysis (A)” menu, select “SF plot” and the screen will show the following SF plot windows. The program will execute an SF plot from adsorption data of an isotherm.

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).

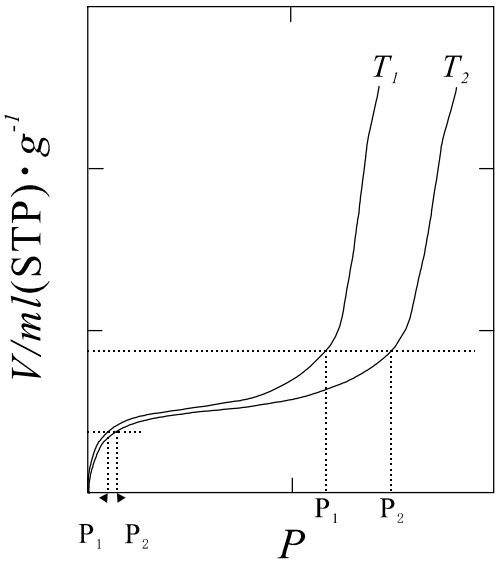
$$\left(\frac{\partial \ln P}{\partial T}\right)_{n_a} = -\frac{\Delta H_{ads}}{RT^2} = \frac{q_{st}}{RT^2} \tag{25.9}$$

$-\Delta H_{ads}$ 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) .

$$q_{st} = \frac{RT_1T_2}{T_2 - T_1}(\ln p_2 - \ln p_1) \tag{25.11}$$

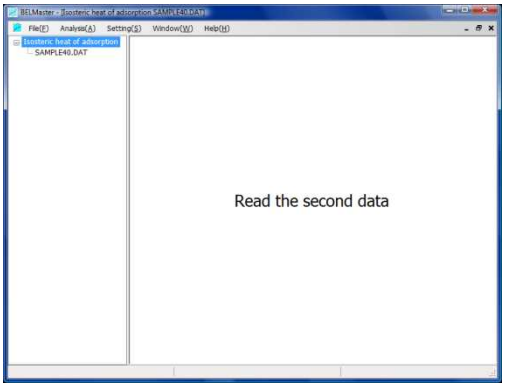


Heat of adsorption is closer to heat of condensation where adsorption amount is large. Heat of adsorption at low adsorption amount is important for the surface characteristic study. However, in the method that uses Clausius-Clapeyron equation, the difference in pressures is so small at low adsorption 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.

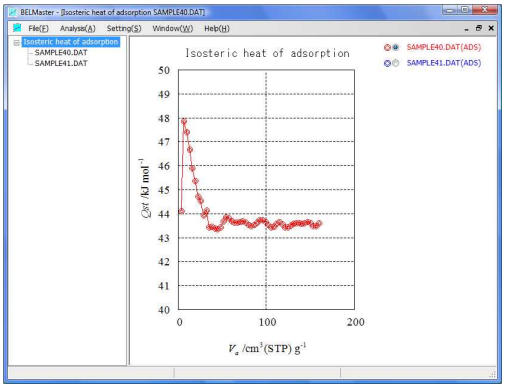
25-2. Operation

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”.

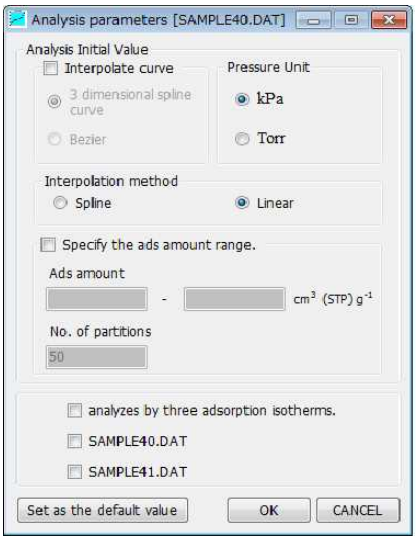


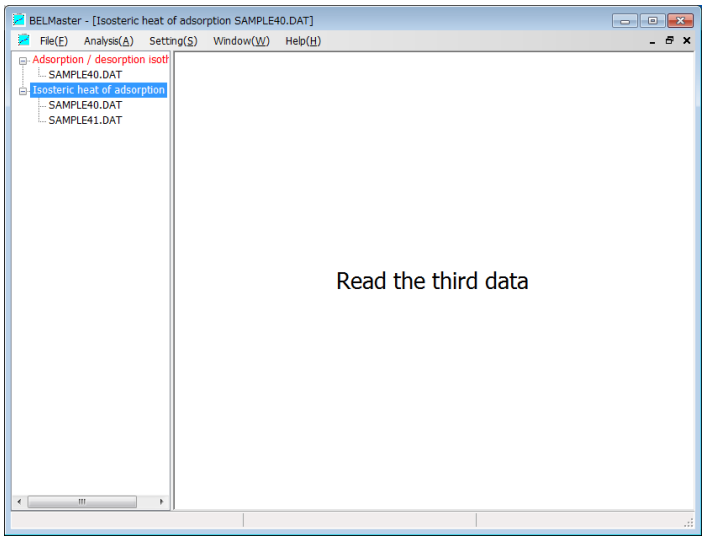
2. On the BEL analysis program menu, or the menu displayed by clicking the mouse right button, select “Read additional data” and then read the 2nd set of data.

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.



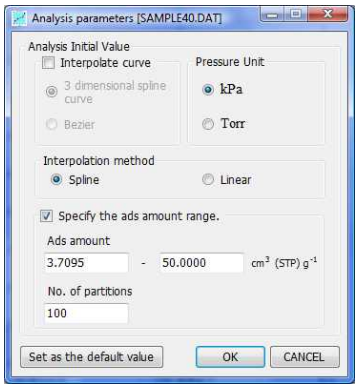
To execute analysis with three isotherms, select [Read additional data] in the analysis software menu, or in the sub window right-click menu, and read data on the third isotherm. Also, selecting [Analysis with three adsorption isotherms] in [Analysis parameters] enables analysis with three isotherms.



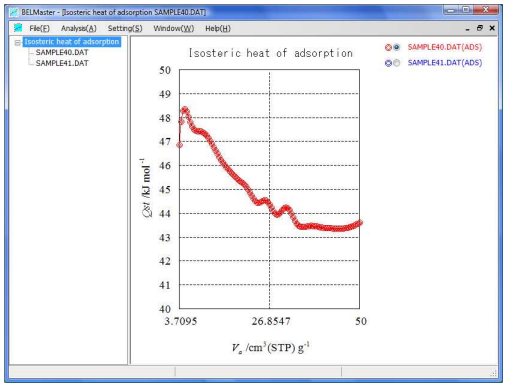


4. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown right will appear. Change the settings as needed.

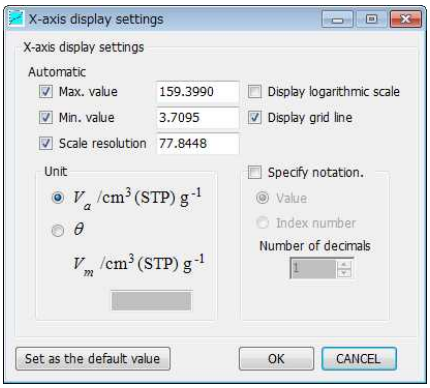
   When “Specify the ads amount range” is selected, the program will calculate the Isosteric heat of adsorption specified in the table below (“ads amount” and “No.of partitions (5 ≤ “No. of partitions ≤ 500)).



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).



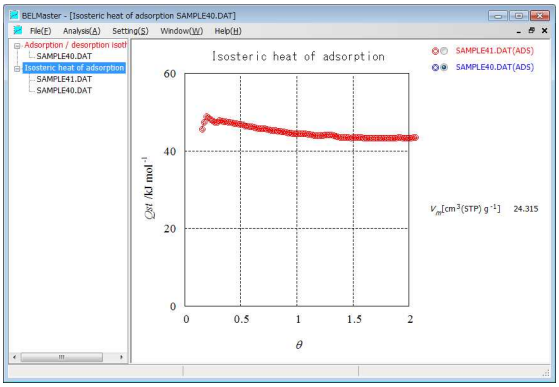
6. For analysis of isosterioc heat of adsorption, “*Va/cm³ (STP) g⁻¹*” or “*θ*” can be selected for the X-axis unit in [Setting] – [X-axis setting].



“*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.



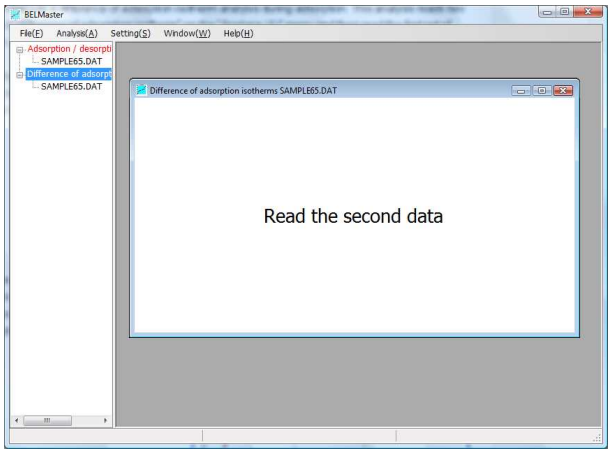
Chapter 26: Difference of adsorption isotherm

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.

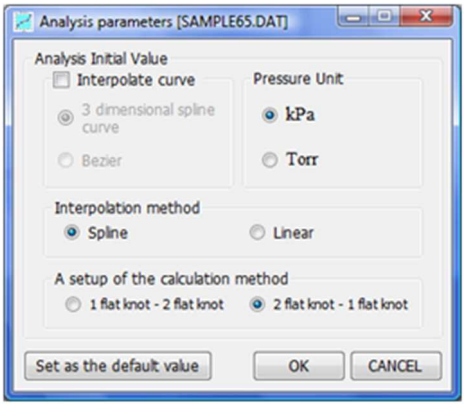
26-2. Operation

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”.

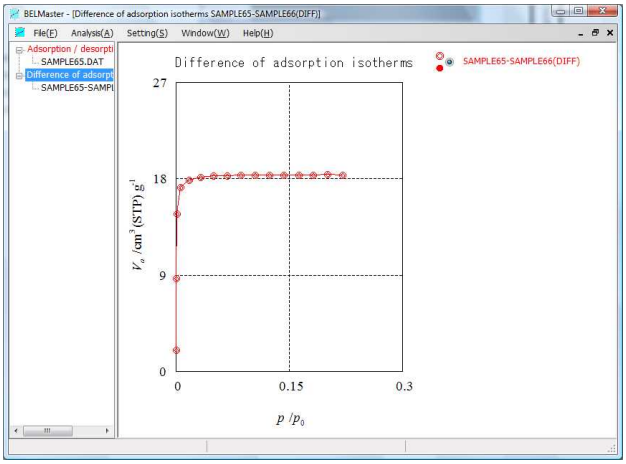


2. On the BEL analysis program menu, or the menu displayed by clicking the mouse right button, select “Read additional data” and then read the 2nd set of data.

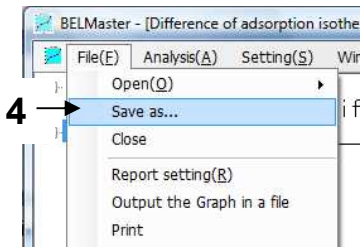
3. Select “Analysis parameters” on the “Setting” menu and the “Analysis parameters” window shown on the right will appear. Change the settings as needed.



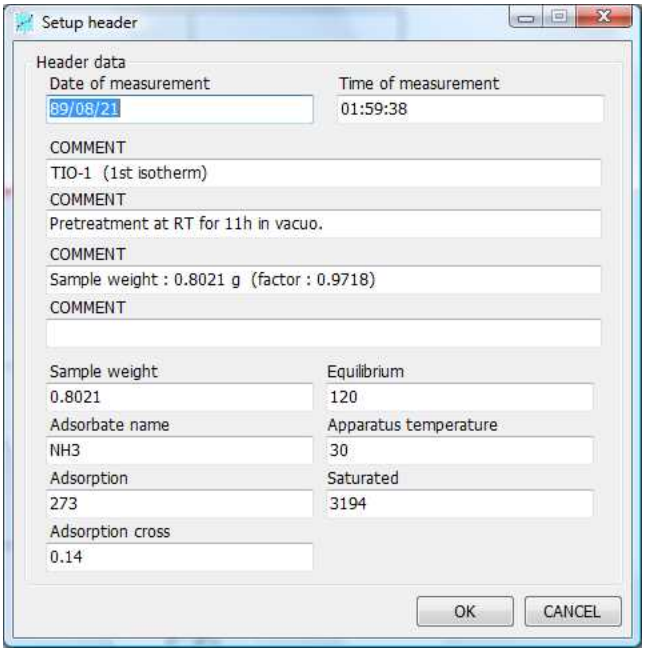
4. Obtain the difference of adsorption isotherm from these two sets of data. The program obtains the adsorption volume of the 2nd set of data by interpolating it with the relative pressure from the 1st set of data. The figure on the right is the result of measuring ammonia adsorption (1st and 2nd adsorption trials) by titanium oxide. The chemical adsorption of ammonia by titanium oxide can be calculated as 18.4 $cm^3(STP)g^{-1}$.



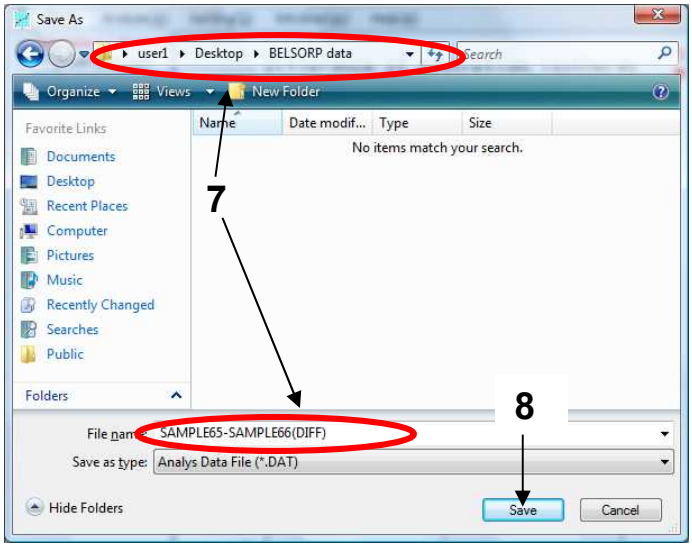
5. The data obtained from a “difference of adsorption isotherms” can be saved in an “adsorption isotherm” file. The data can later be analyzed using other analysis methods like a Langmuir plot. To save a difference of adsorption isotherm, select “File (F),” and then “Save as”.



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.

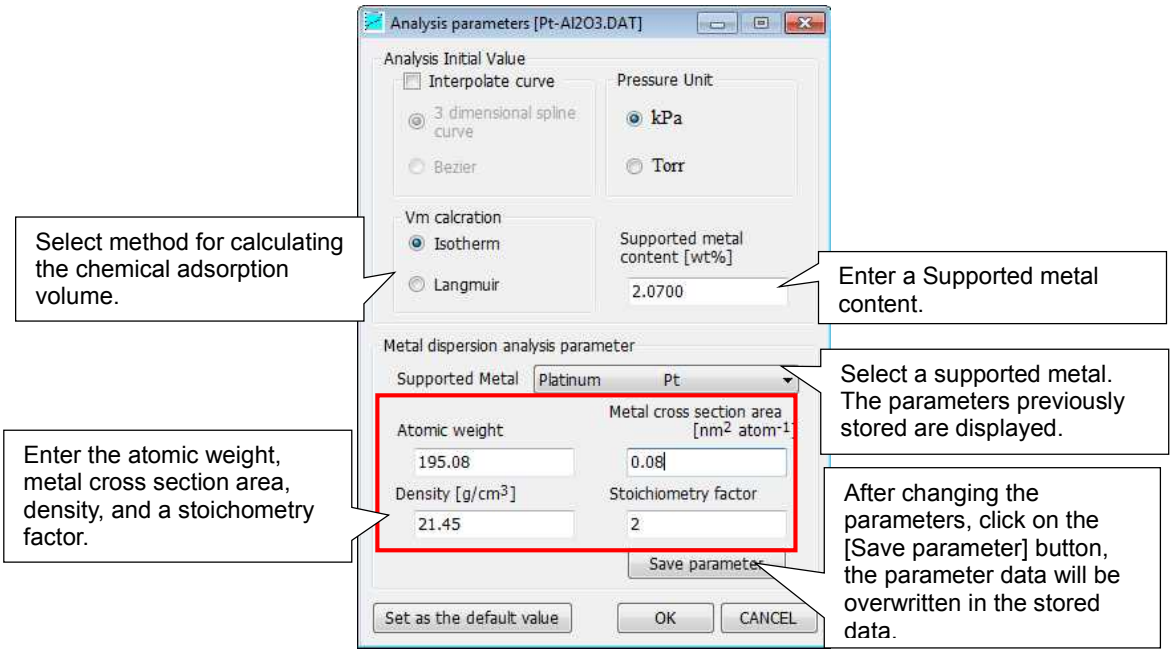
There are various ways to evaluate cross-sectional area of supported metal, and many values are listed in literatures. The following table indicates some examples that were calculated from average surface atom concentration, which are described in a literature (Catalyst course(additional volume), Catalyst 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

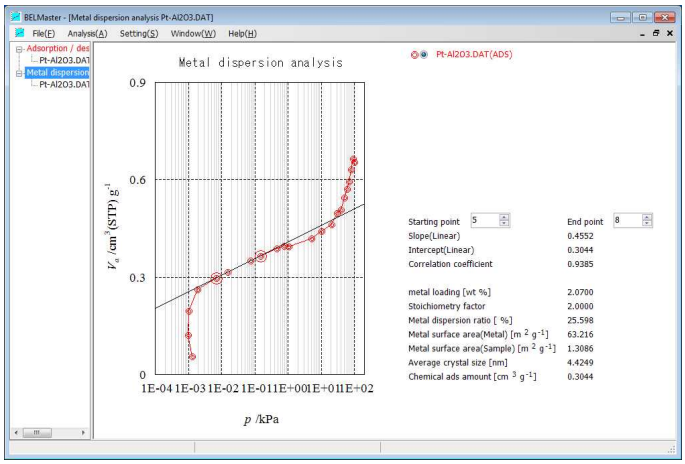
27-2. Operation

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.

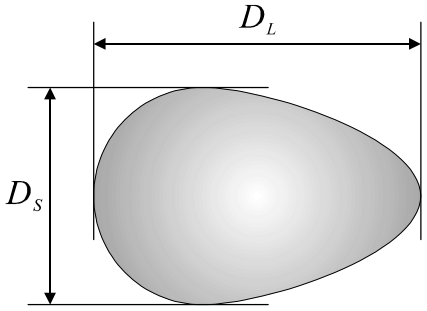


Chapter 28: Molecular probe method

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.).

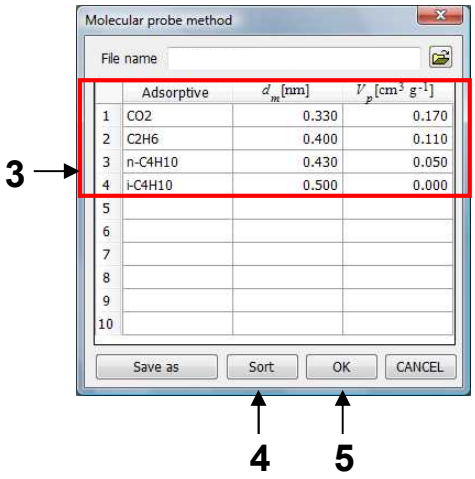


28-2.

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.

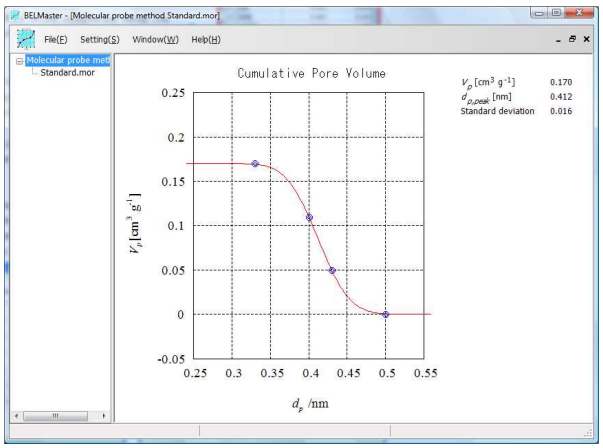
2. Select a “Molecular probe method” on the “Analysis (A)” menu. The “Molecular probe method” numerical data window shown below will appear.

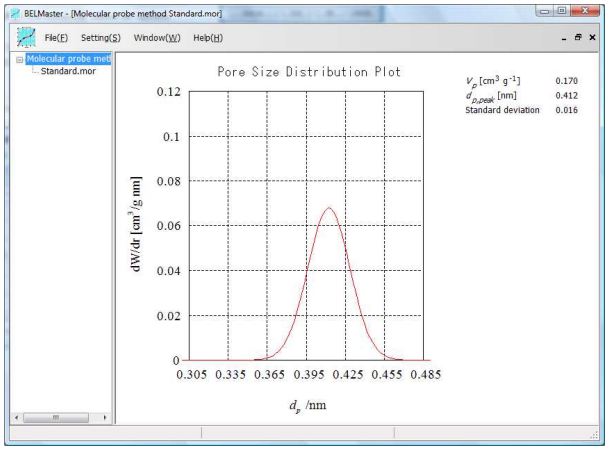


3. Enter an “Adsorbate name,” “d_m (adsorbate molecular diameter),” and “V_p (pore volume)”. If molecular probe analysis data is already stored, click  and you can select a file. Change the numerical values as needed.

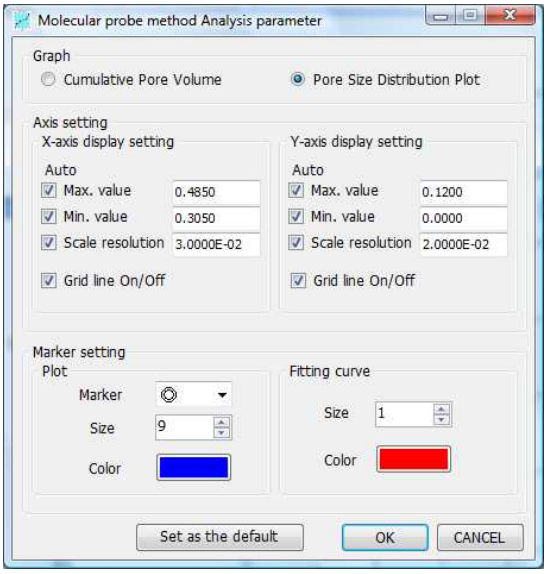
4. Click on the [Sort] button, the program will sort data in order of larger to smaller d_m (adsorbate molecular diameter). Click on the [Save as] or [OK] button and the program will sort the data automatically.

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”.

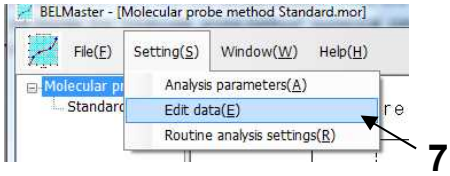




6. On the analysis menu, select “Setting” and “Analysis parameter,” the screen will show the “Molecular probe method Analysis parameter” window. You can select graph type, specify X and Y axes, and markers.

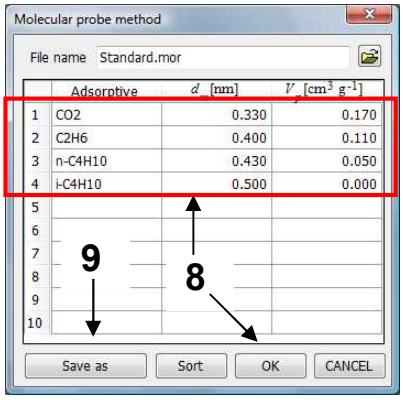


7. Select “Setting(S)” and “Edit data (E)” on the analysis menu and the program will display the “Molecular probe method” numerical data window. You can modify the molecular probe data in this window.



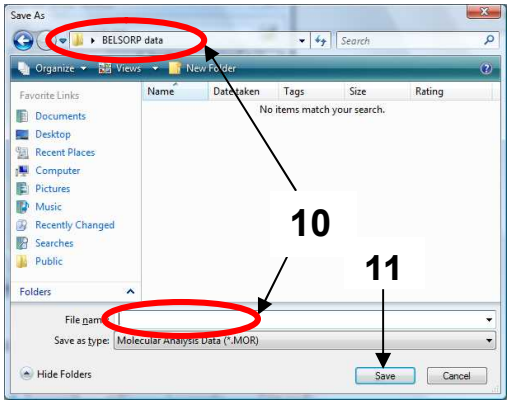
8. After changing the data, click on the [OK] button, and check the graph that is displayed.

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.

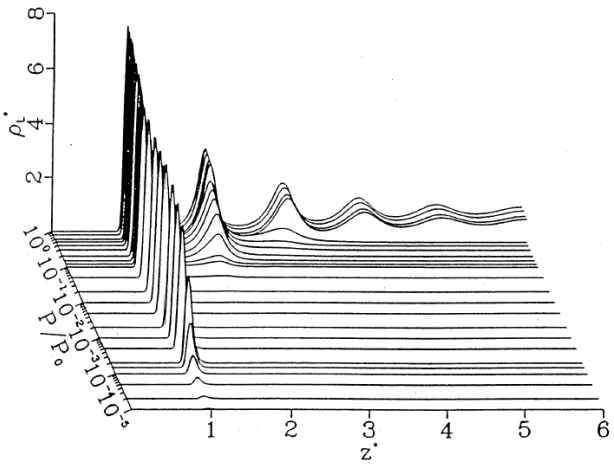


Fig. 1: Localized Density Profile using NLDFT
(P/P_0: Relative pressure, ρ_L*: Local density, Z*: Distance from carbon atom on graphite surface)

• 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.

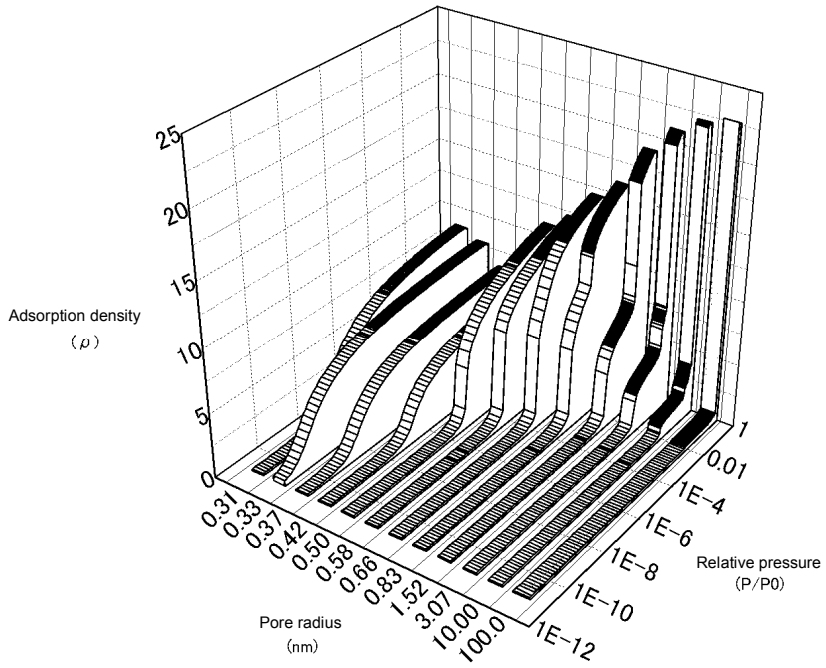


Fig. 2 Theoretical Density Adsorption Isotherm
(Parameters: Cylindrical pore, Adsorptive molecule: Ar, Pore surface atom: O)

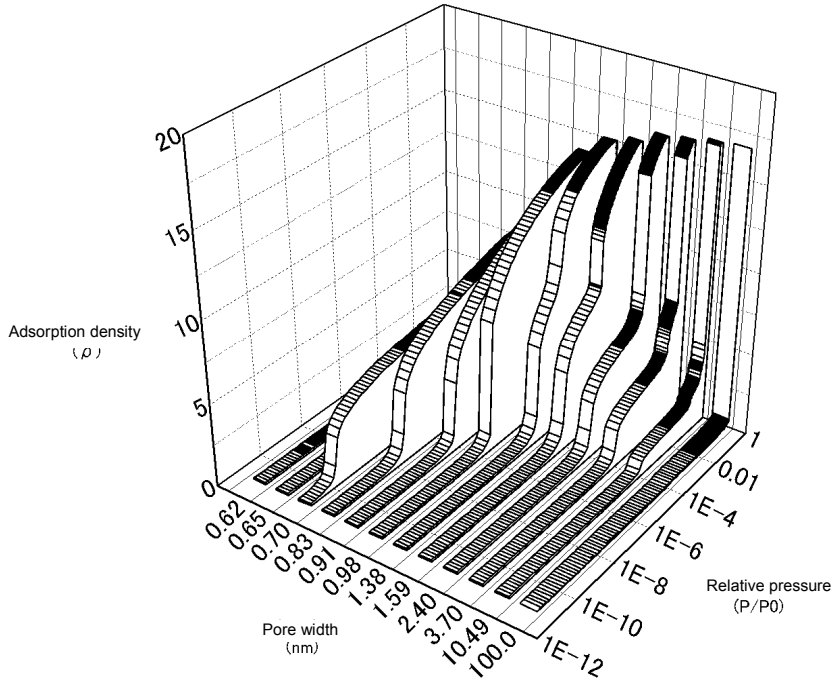


Fig. 3 Theoretical Density Adsorption Isotherm
(Parameters: Slit-shaped pore, Adsorptive molecule: N_2, Pore surface atom: C)

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.

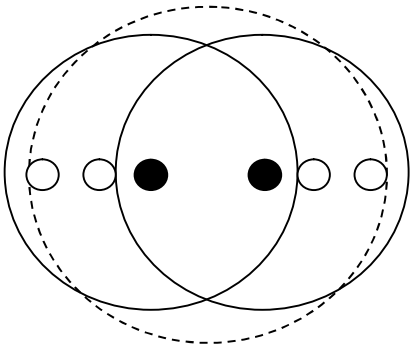


Fig. 4 Modeled N_2 molecule, -hard sphere system of DFT, -for GCMC (●: LJ center lx, ○: charge center lq)

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.

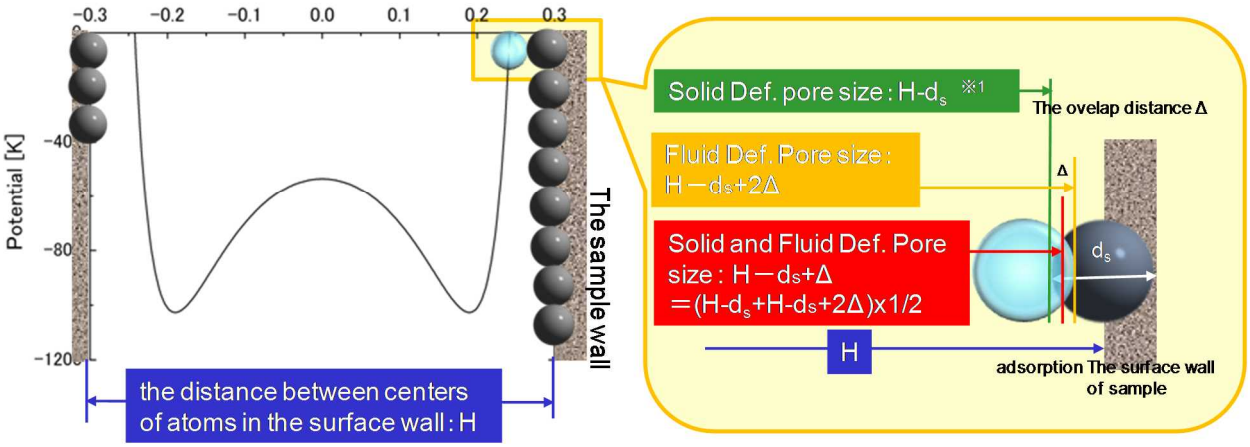
6) Definition of pore diameter

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.



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3) Seaton, N.A., Walton, J.R.B., Quirke, N., *Carbon* **27,** 853 (1989).
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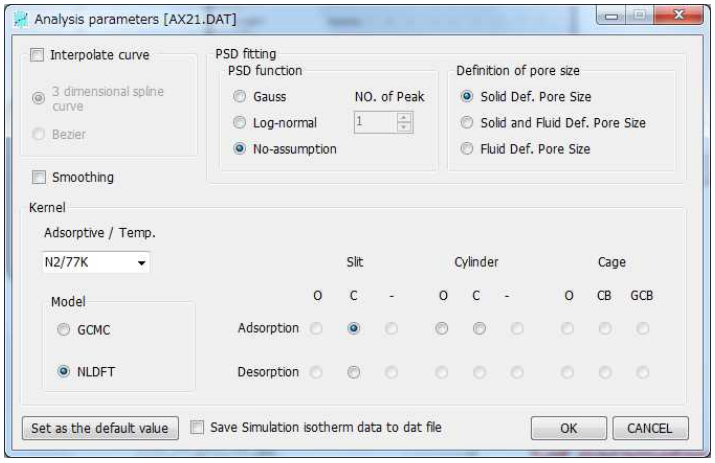
10) Ravikovitch, P.I., Vishnyakov, A., Russo,R., Neimark, A.V., *Langmuir* **16**, 2311 (2000).
11) “Nitrogen Adsorption in Slit Pores at Ambient Temperatures: Comparison of Simulation and Experiment”, K. Kaneko, *Langmuir,* **10**, 4606 (1994)
12) ”A STATISTICAL MECHANICS INTERPRETATION OF THE ADSORPTION 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.

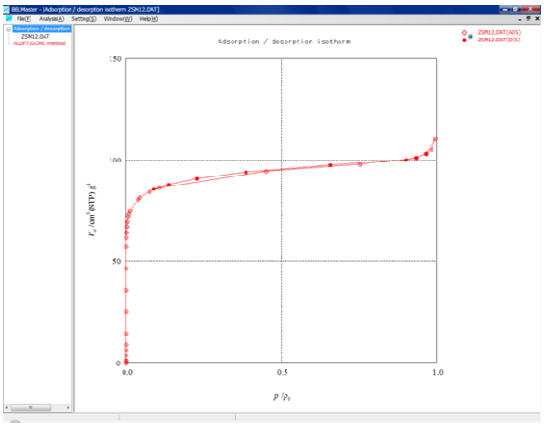
  We currently offer the kernel described later.

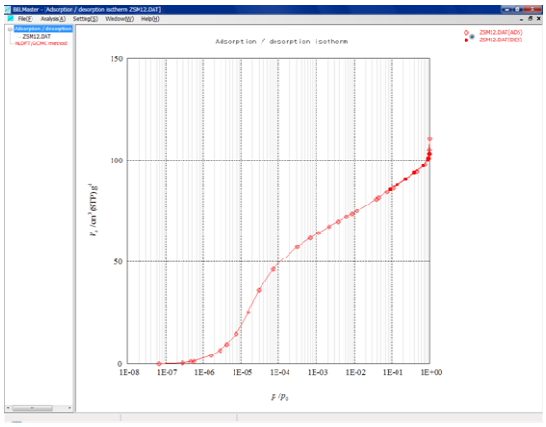
		Slit			Cylinder		
NLDFT	N_2 77 K	O	C	-	O	C	-
		-	O des.	-	O	O	
	Ar 87 K	O	CB	GCB	O	CB	GCB
		-	-	-	O	O	O
	CO_2 298 K	O	C	-	O	CB	GCB
		-	-	-	-	-	-
GCMC	N_2 77 K	O	C	-	O	C	-
		-	O des.	-	O	O	
	Ar 87 K	O	CB	GCB	O	CB	GCB
		-	-	-	O	-	-
	CO_2 298 K	O	C	UMPC*	O	CB	GCB
		-	O	O	-	O	O

  It is suitable for the analysis for 0.1 MPa (pore width 0.32 – 1.5 nm) or less

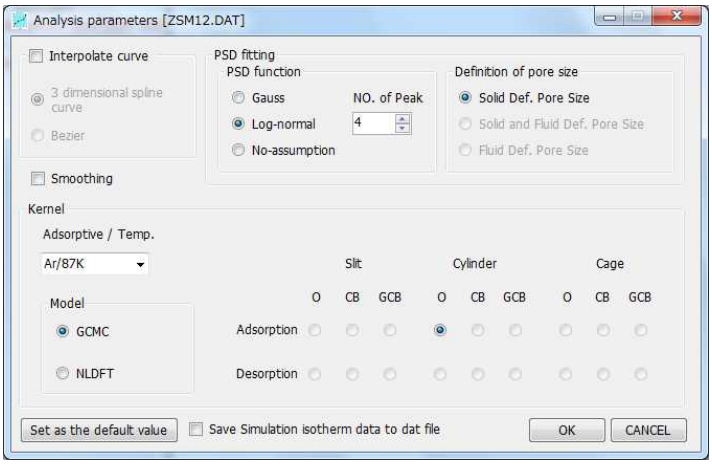
2. After specifying the analysis parameters, press the [OK] button to start calculation. After calculation is completed, a pore distribution curve and ideal adsorption isotherm data are displayed.

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.

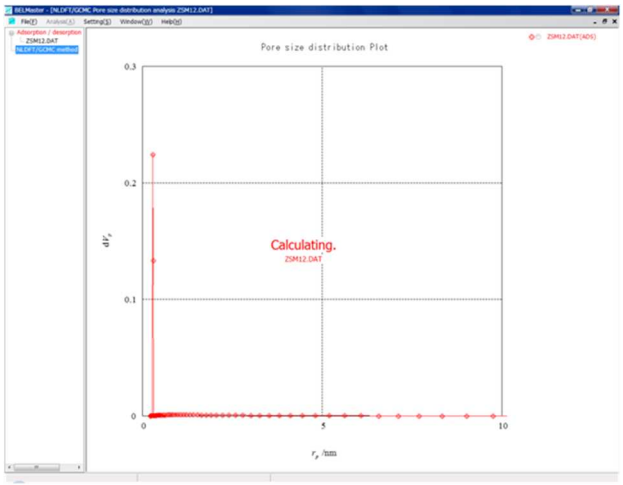




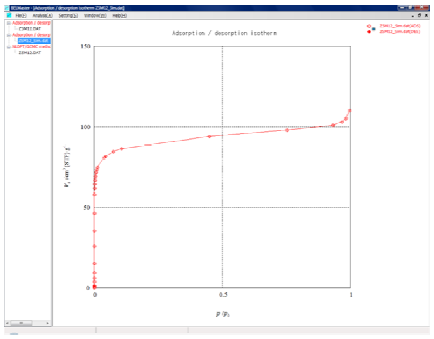
4. Specify the analysis parameters as shown on the right. These data are intended for GCMC analysis. Press the [OK] button to start calculation. (Analysis conditions: Distribution function: log-normal, Number of peaks: 4, Cylindrical, Oxygen, Ar/87 K)



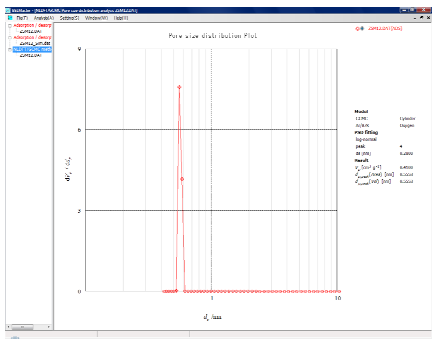
5. During calculation, the window as shown on the right is displayed.



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”.

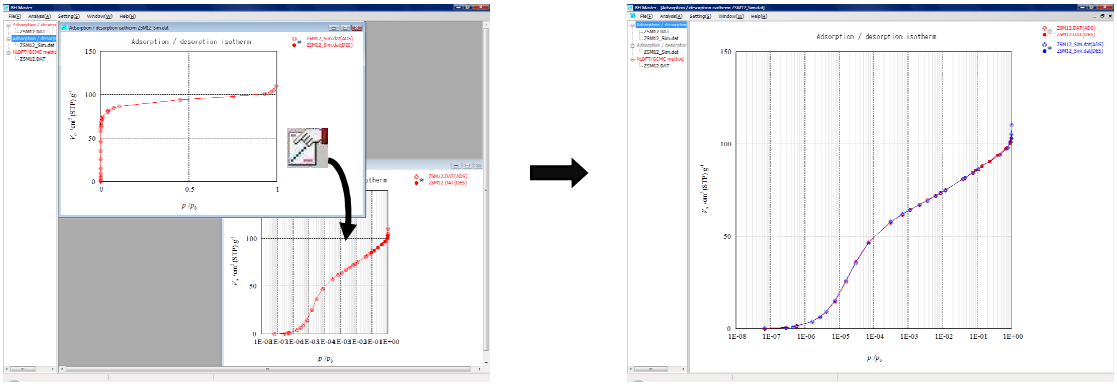


Ideal adsorption isotherm

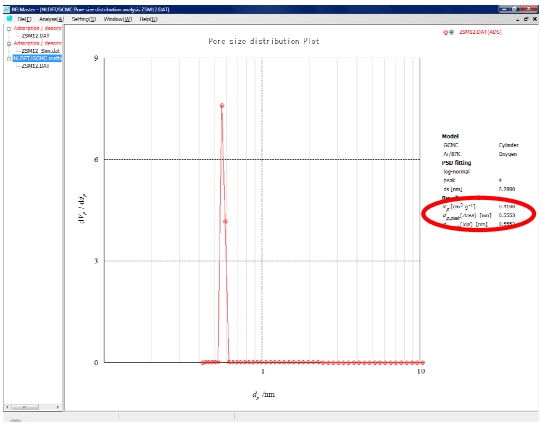


Pore distributiona curve

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.

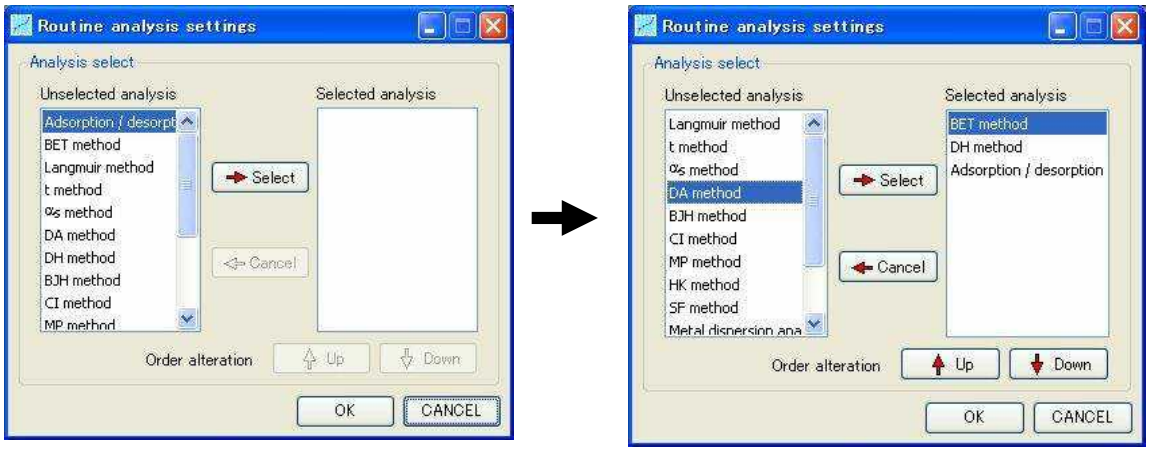
Chapter 30: How to use [Routine analysis]

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.

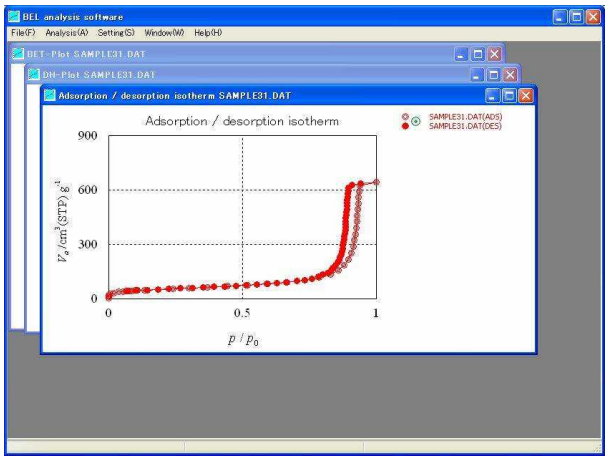
2. Select analyses you want to use from the “Unselected analysis” list. Then click on the [Select] button. The selected analysis names will be moved to the “Selected analysis” list. These are now added to the selected analyses.



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

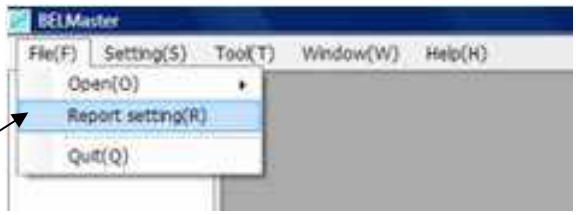
You can output numerical data or graphs as an Excel file (*.XLS), and can be edited with Excel. This function is useful to prepare reports. For equivalent weight differential heat of adsorption, difference adsorption isotherm, and molecular probe method, the analysis report output function is disabled.

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.

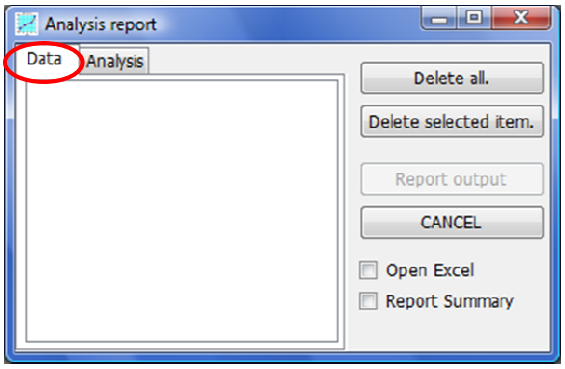
31-1. Operation

1. Select “Report settings” in the “File” menu.

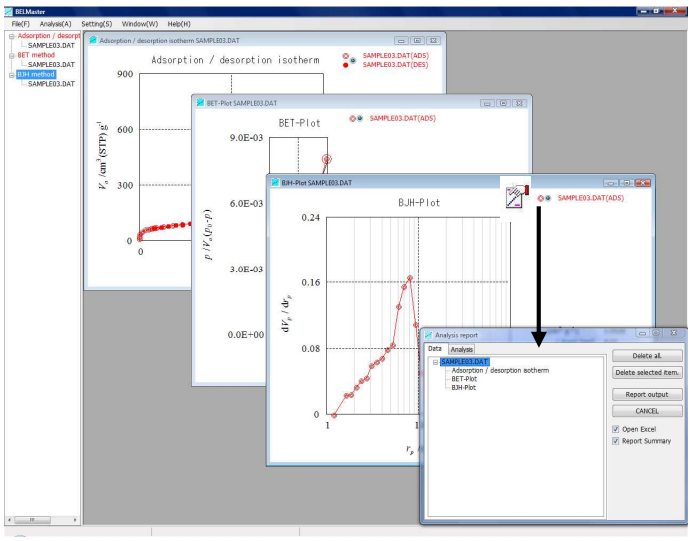


2. The “Analysis report” window appears as shown on the right.

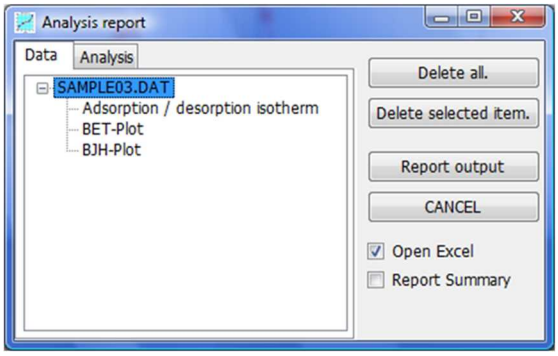
To output a report of several analysis results with the same data, select “data”.



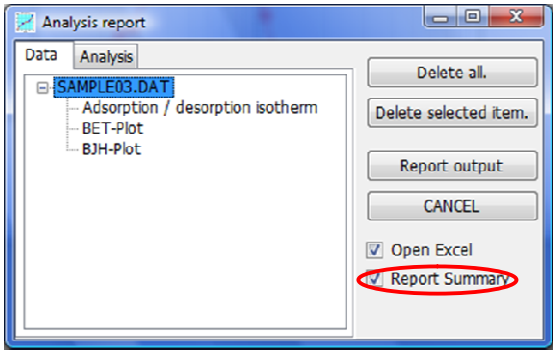
3. Drag and drop analysis data from a desired analysis window into the “Analysis report” window to copy the analysis data. The data at the time of copying will be output in an analysis report. After the data is copied, any setting change will not be reflected in the report.



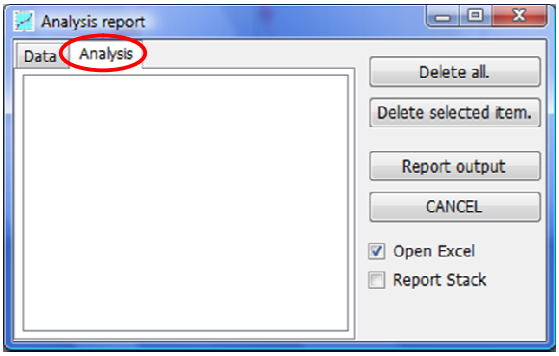
4. After the data is copied, the Analysis report settings window is displayed as shown on the right.



5. If the “Report Summary” checkbox is checked, a summary report will be prepared.

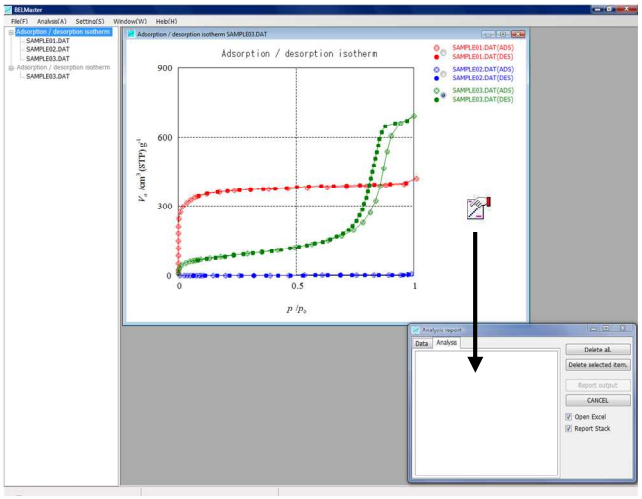


6. When two or more data are displayed in a single graph, or a report output of analysis results of the same analysis method from different files, select “Same analysis”.

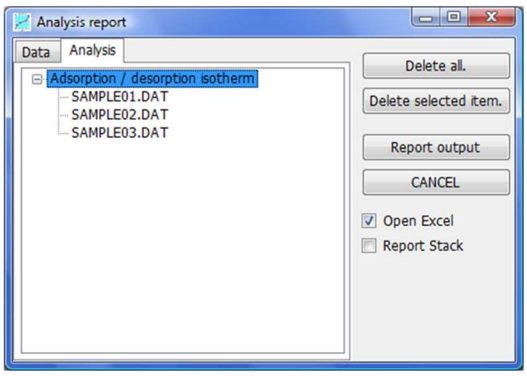


7. Drag and drop analysis data from a desired analysis window into the “Analysis report” window to copy the analysis data.

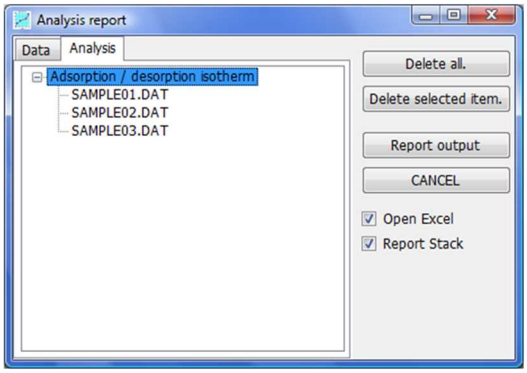
The data at the time of coping will be output in an analysis report. After the data is copied, any setting change will not be reflected in the report.



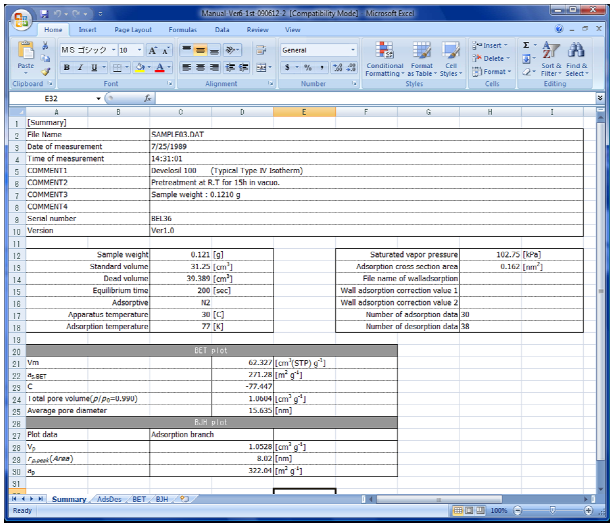
8. After the data is copied, the Analysis report window is displayed as shown on the right.



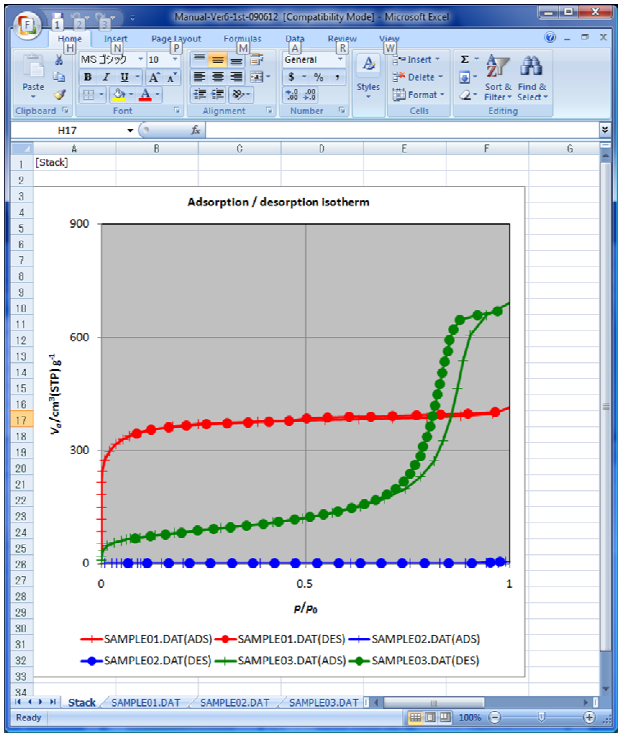
9. To output an overlap graph, mark an “Report stack” checkbox.



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.

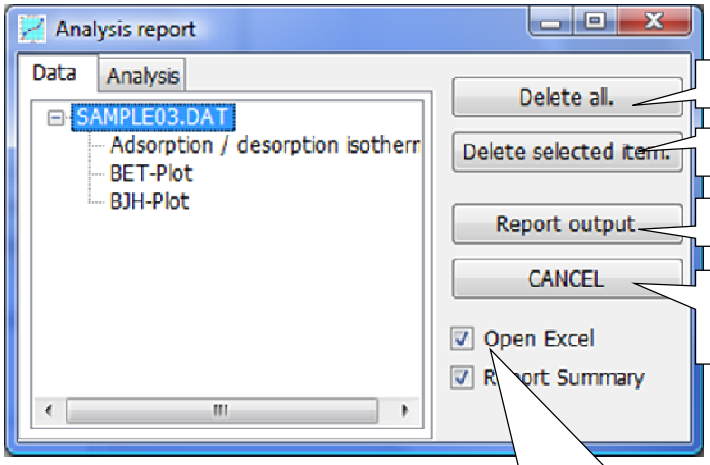


Report summary



Report stack

11. Other functions of the “Analysis” window are as follows:



Deletes copied data.

Deletes a selected item only.

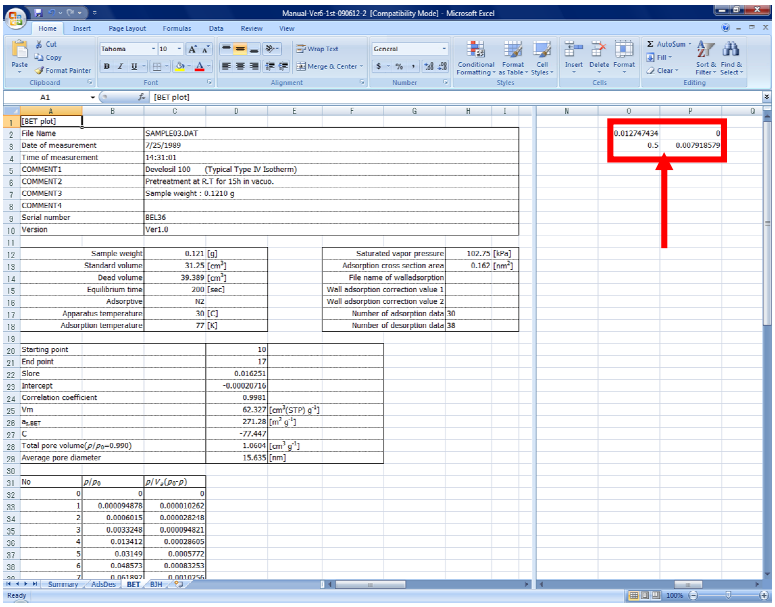
Outputs an analysis report.

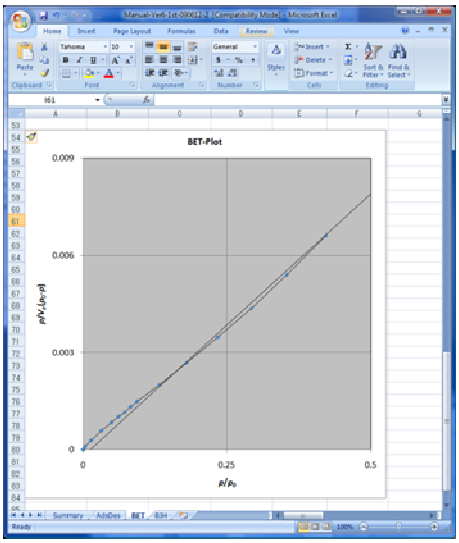
Closes the “Analysis report” window.

When this checkbox is ON, Excel will open after an analysis report is output.

—Output of report—

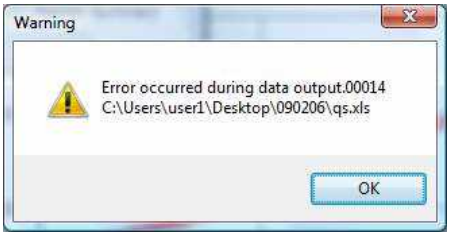
Using two points in least-squares method, the start point and end point of BET-plot, Langmuir plot, t plot, α_s plot, DA-plot, are displaid in these plot output report as shown below. Top step is the start point and bottom step is the end point.





31-2. Setting change

When you use “Analysis report” function, an error (00014) might be displayed as below.

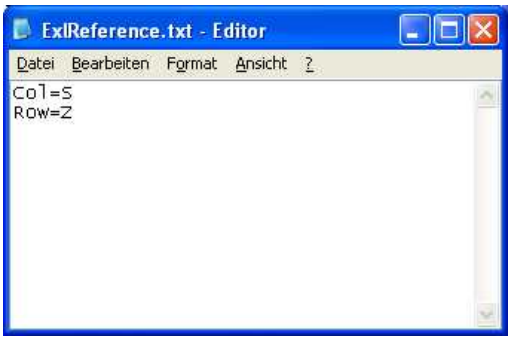


Refering to a cell within an Excel worksheet, a reference style where both the rows and the columns on the worksheet are numbered can be used. (In English version, the style is called “R1C1” reference style). This style is different in linguistic versions of Excel and the error 00014 is caused. In this 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).

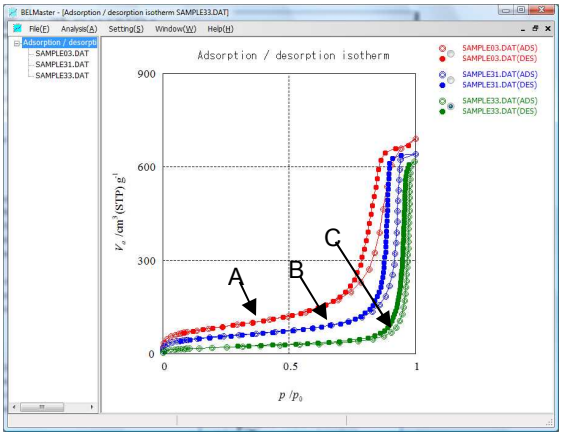
2. These adsorption isotherms display hysteresis (a part that does not match between adsorption process and desorption process), and are type IV adsorption isotherms.

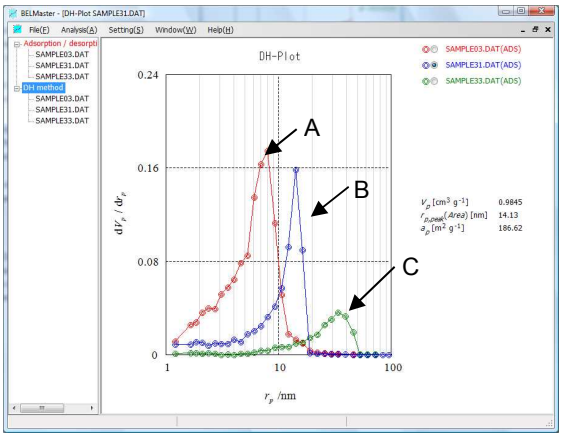
3. From these conditions, we can determine that these samples have mesopores.

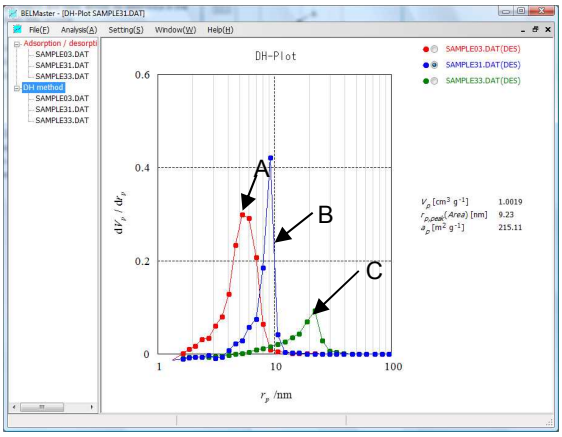
4. Since mesopore analysis theory is based on the Kelvin equation, the BJH plot, DH plot, and CI plot are suited for analysis. They are all based on the capillary tube condensation theory, and have almost no difference in the analysis results they provide.

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.

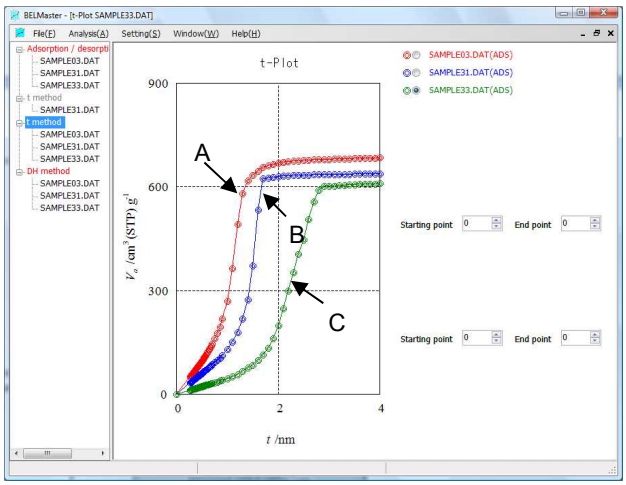
6. When the DH plot is used to the desorption process, the result is shown in the figure on the right, the pore distribution in the neck area (thinner part) can be obtained from the desorption process.







7. The figure on the right is the analysis result of a t -plot.

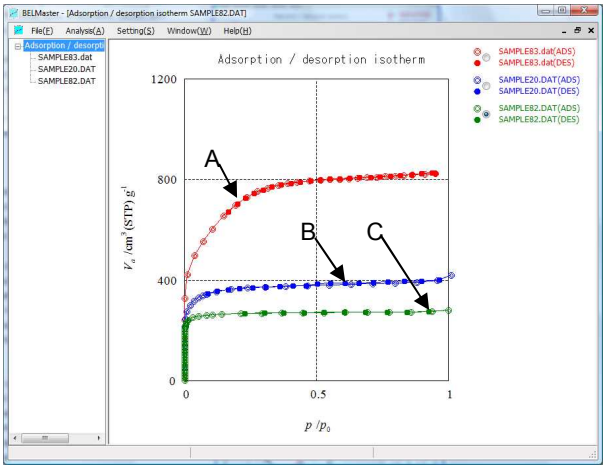


8. Data obtained using the BET plot, DH plot, and t plot are shown in the table below. We can evaluate sample information (specific area, pore volume etc.) from more than one analysis.

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.

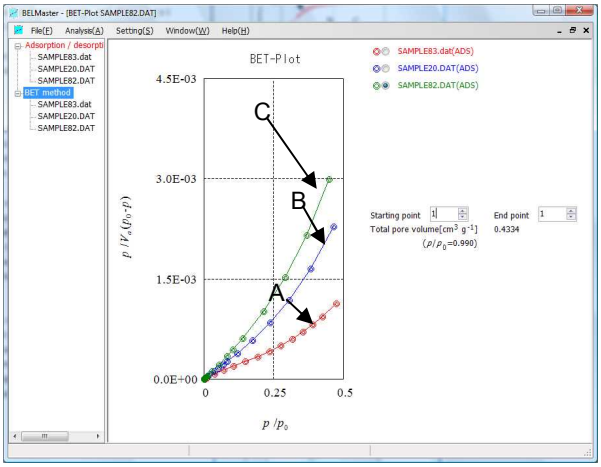


2. These adsorption isotherms have high adsorption volume at a relative low pressure range, and show a type I adsorption isotherm.

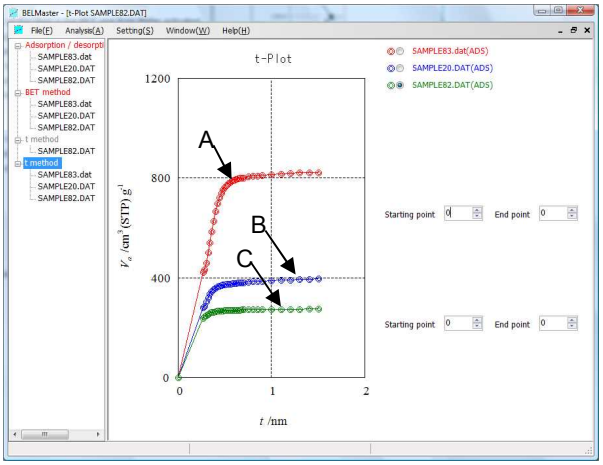
3. From these conditions, we can determine that these samples have micropores.

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.

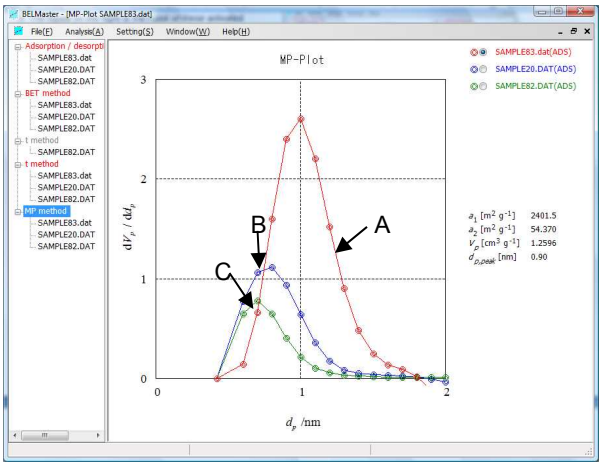
5. The figure on the right is the BET plot from these activated carbons. Activated carbon C has the smallest pore diameter, and the deviation from a straight line is large. Select the range for the straight line so that the C value will be a positive value at relatively low pressure. Then calculate the specific area.



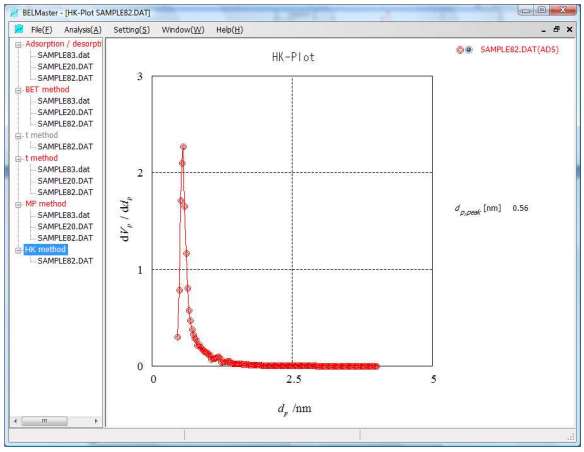
6. The figure on the right is the t-plot of these activated carbon samples. It is difficult to obtain the total specific area for activated carbon C. Also, as the pore diameter get smaller, the result may be greatly affected by the micropore effect and the total specific surface value will be larger 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.

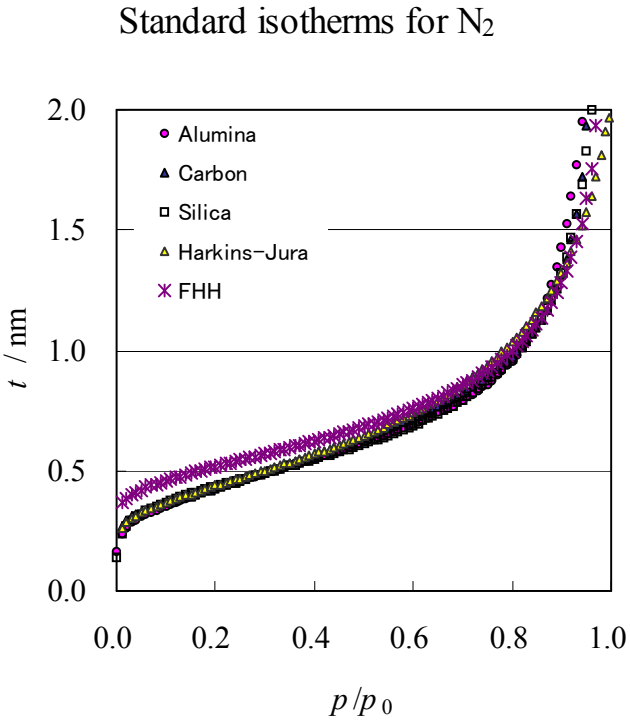


Figure1: Standard isotherm using BEL SORP analysis program

$$t = 0.1 \times \left[\frac{13.99}{0.034 - \log_{10}\left(\frac{p}{p_0}\right)} \right]^{\frac{1}{2}} \quad (1)$$

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

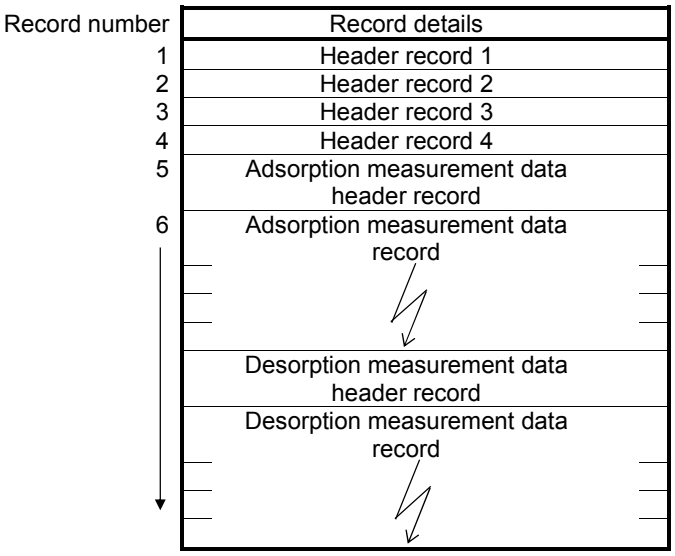
BEL SORP series “measurement data” are stored at each measurement step. During measurement, a “measurement data” file can be opened using this analysis program, and data can be analyzed, so that you can always see the measurement conditions.
In addition, the “measurement data” file is a text format file 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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