Analysis Software

BELMaster^{TM}

User’s Manual

Thank you for purchasing this product.

- Read the user's manual thoroughly, and then use the software correctly.
- **Before use, be sure to read "PRECAUTIONS (pages 1)."**
- After reading the user's manual, store it safely in a location where it can be accessed whenever necessary.

PRECAUTIONS

About this manual

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  http://www.nist.gov/srd/nist23.cfm

CONTENTS

Introduction

BELSORP analysis software

The following sample information about surface areas and pores can be obtained from the measured data.

Name of analysis	Adsorptive	About analysis method	Primary analyzed data
Adsorption/desorption isotherm	Isotherms 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.		
Adsorption rate	N_2、Ar、H_2 etc.	Evaluation of adsorption rate	Mass transfer coefficient Surface diffusion coefficient
PCT curve	H_2	Change in amount of hydrogen storage capacity	Amount of hydrogen storage capacity
BET plot	N_2、Ar、Kr etc.	Evaluation of specific surface area for physical adsorption	Monomolecular layer adsorption
Langmuir plot	O_2 etc.	Evaluation of chemisorption amount	Monomolecular layer adsorption
Freundlich plot	N_2、Ar、Kr etc.	Evaluation of specific surface area for physical adsorption	Monomolecular layer adsorption
t plot	N_2 etc.	Evaluation of micropores	Total specific surface area External specific surface area Pore volume
α_s plot	N_2 etc.	Evaluation of micropores	Total specific surface area External specific surface area Pore volume
MP plot	N_2 etc.	Micropore distribution curve	Micropore distribution
BJH plot	N_2 etc.	Mesopore distribution curve	Mesopore size distribution, volume and area

CI plot	N_2 etc.	Mesopore distribution curve	Mesopore size distribution, volume and area
DH plot	N_2 etc.	Mesopore distribution curve	Mesopore size distribution, volume and area
INNES plot	N_2 etc.	Mesopore distribution curve	Mesopore distribution, volume and area
DA plot	N_2、CO_2、C_6H_6 etc.	Evaluation of micropore volume	Micropore volume
Metal dispersion	H_2、CO etc.	Evaluation of metal dispersion	Metal dispersion
HK plot	N_2、Ar, CO_2	Micropore distribution curve	Micropore size distribution (Pore shape: Slit)
SF plot	N_2、Ar	Micropore distribution curve	Micropore size distribution (Pore shape: Cylinder)
CY plot	N_2、Ar	Micropore distribution curve	Micropore size distribution (Pore shape: Cage)
Isosteric heat of adsorption	H_2O etc.	Evaluateion isosteric heat of adsorption	Isosteric heat of adsorption
Fractal dimension	N_2、Ar、H_2O etc.	Evaluation of fractal surface dimension	Surface fractal dimension
Difference of adsorption isotherms	H_2O、NH_3 etc.	Evaluation of chemisorption amount	Difference of adsorption isotherms
Molecular probe	CO_2、C_2H_6、n-C_4H_{10}、iso-C_4H_{10} etc.	Micropore distribution curve	Micropore size distribution
NLDFT/GCMC	N_2、Ar、CO_2	Evaluation from micropores to macropores	Pore size distribution

Folder configuration of the analysis software

The folder configuration right after the software is installed is as follows. Please note that, if some files are not in the specified folders, the analysis software may not operate normally.

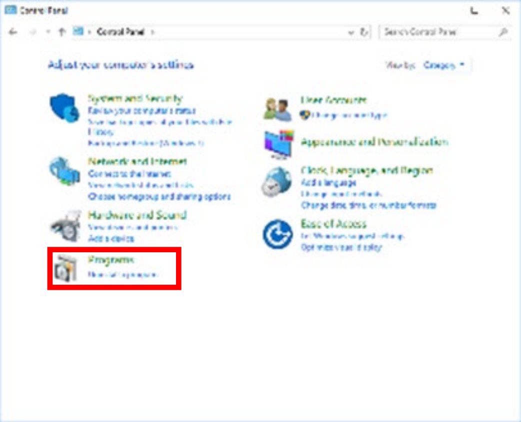
Folder configuration	Description	Details
BELMaster7	Installation folder	A different folder name can be used.
BELMaster.exe	Execution file	
*.dll	Expansion file used by the execution file	Be sure to place this file in the same folder as the execution file. Note: If you delete the expansion file, this 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] 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.
ADSORPTIVE_DEFAULT.csv	Adsorptive default file	Be sure to place this file in the same folder as the execution file.
DefultHeader.bmp	Print header file	This file is used for header file in printing the data. Be sure to place this file in the same folder as the execution file.
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, α_s 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 α_s 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.
*.CYS	CY method parameter	Indispensable for the CY 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.
NLDFT	NLDFT / GCMC folder	Be sure to place this file 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 simulation analysis.

Uninstalling the analysis software

This chapter describes the steps to uninstall the BELMaster7 analysis software.

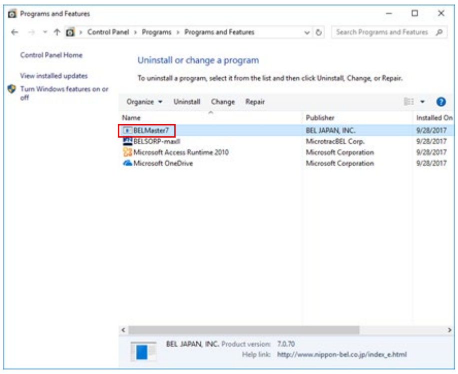
Uninstalling the analysis software

1 Open the Windows “Control Panel”.



2 Click on the “Uninstall a program”.

3 Select the “BELMaster7 analysis software” from the list of programs shown and click on the Uninstall button.



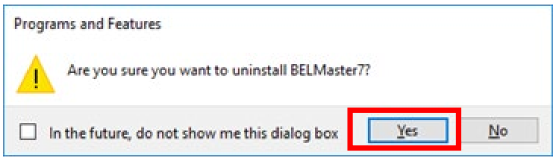
Uninstall or change a program

To uninstall a program, select it from the list and then click Uninstall, Change, or Repair.

Name	Publisher	Installed On
BELMaster7	BEL JAPAN, INC.	9/28/2017
BELSORP-maxII	MicrotracBEL Corp.	9/28/2017
Microsoft Access Runtime 2010	Microsoft Corporation	9/28/2017
Microsoft OneDrive	Microsoft Corporation	9/28/2017

BEL JAPAN, INC. Product version: 7.0.70
Help link: http://www.nippon-bel.co.jp/index_e.html

4 Click the Yes button in the “EXEpress Uninstaller” window.



Programs and Features

Are you sure you want to uninstall BELMaster7?

☐ In the future, do not show me this dialog box

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 analysis software has been uninstalled.

Basic Operation

Starting and ending the software

This chapter describes how to start and end the BEL analysis software.

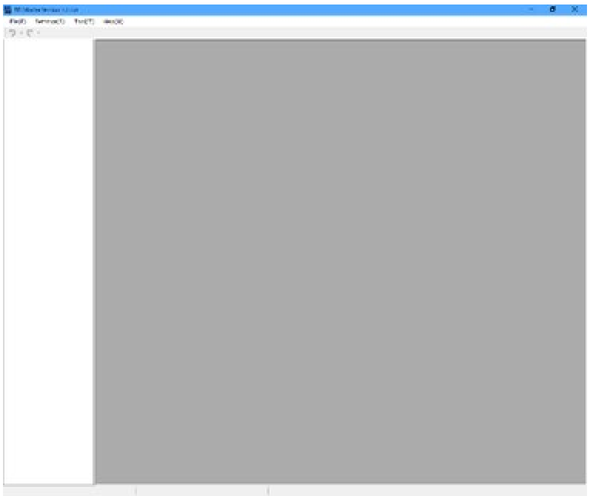
For details about basic Windows operations, see the Windows instruction manual. Depending on your system’s environment, the screen images on your PC may be different from the images shown in this manual.

Start up

1 Turn on your computer and start Windows.

2 From the "Start" bar select "All Programs", select BELMaster7(TM).

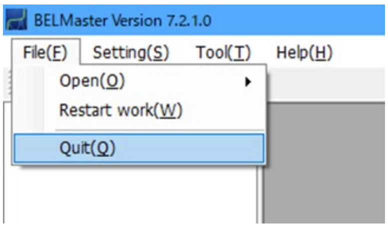
3 The BEL analysis software will start and the main window, shown on the right, will appear.



Quit

Quitting from main window

Select “File(F)” and then “Quit(Q)” from the main window, that will end the analysis software.

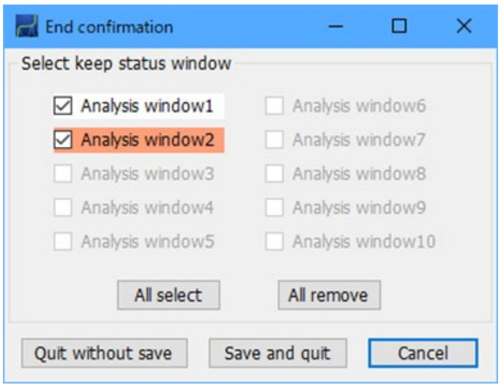


The “End confirmation” window is not displayed.

Quitting from analysis window (in displaying multiple windows)

Since the “End confirmation” window appears, select an analysis window to close after saving the state, and then click the Save and quit button.

To quit without saving, click the Quit without save button.

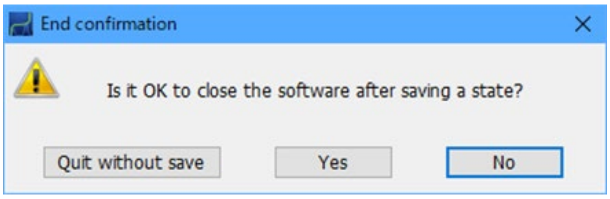


☑ Analysis window1
☑ Analysis window2
☐ Analysis window3
☐ Analysis window4
☐ Analysis window5
☐ Analysis window6
☐ Analysis window7
☐ Analysis window8
☐ Analysis window9
☐ Analysis window10

Quitting from analysis window (in displaying single window)

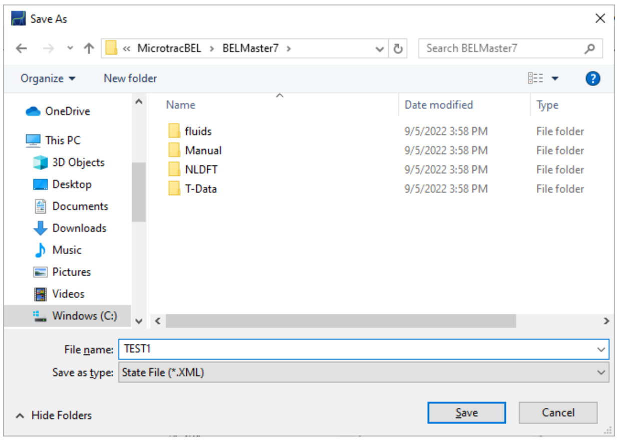
Since the “End confirmation” window appears, click the YES button.

To quit without saving, click the Quit without save button.



Is it OK to close the software after saving a state?

In the case of quitting after saving the state, input the state file name. From the next time onwards, you can select any of the saved state files to resume.

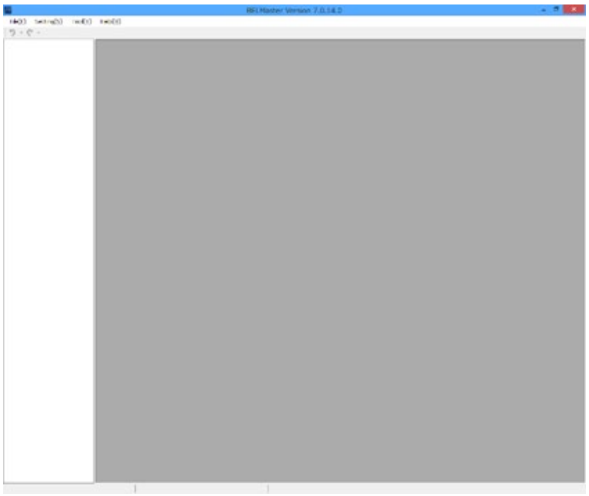
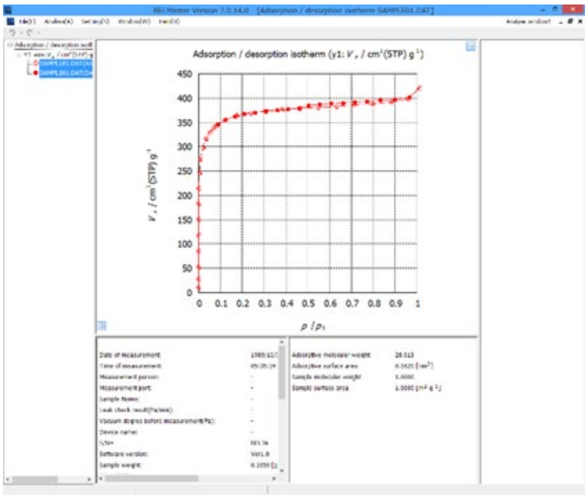
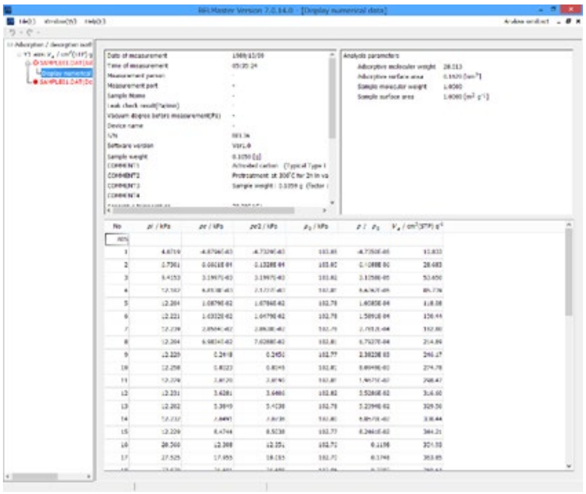


Name	Date modified	Type
fluids	9/5/2022 3:58 PM	File folder
Manual	9/5/2022 3:58 PM	File folder
NLDFT	9/5/2022 3:58 PM	File folder
T-Data	9/5/2022 3:58 PM	File folder

File name: TEST1
Save as type: State File (*.XML)

Window

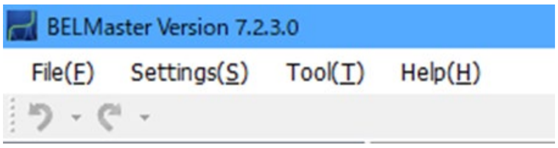
Depending on the analysis conditions, one of three menus will be displayed in the window. This chapter briefly describes the contents of these menus and the function of the items in the menus.

1	Main window (Configures basic settings.)	
2	Analysis window (Displays analysis result.)	
3	Data window (Displays numerical data.)	

Main window

Menu contents

The first menu displayed after starting the BEL analysis software (in the case that no data file is opened)



File	Setting	Tool	Help
Open	Routine analysis setting	Edit data	How to use
Adsorption/desorpotion isotherm	Adsorptive library		Vesion info
Adsorption rate	Language setting		
PCT curve	Unit setting		
⋮	Display setting		
⋮	Print setting		
Restart work			
Quit			

“File” menu

➢ Open

Select “File(F)” → “Open(O)” → “(Analysis method)” to open the analysis window to display analysis data (graph).

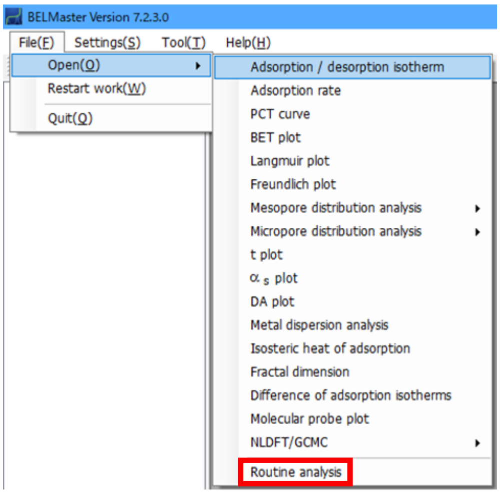
Analysis methods on the menu that are grayed out cannot be selected.

→ Operation P.28 ”Open file”

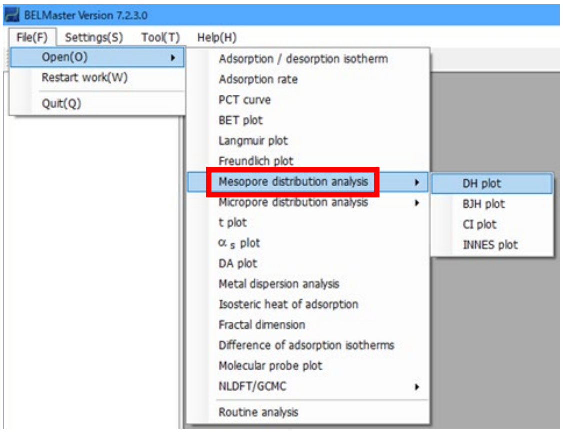
→ Analysis method P.69 "Adsorption/desorption isotherm"～

- Routine analysis
  This function is used to execute multiple analyses at once. The analyses can be specified on the "Routine analysis setting" window.

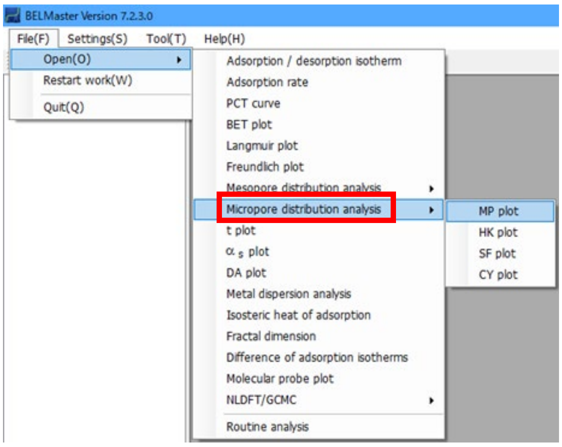
→ Operation P.208 "How to use [Routine analysis]"



- Mesopore distribution analysis
  Choose DH plot, BJH plot, CI plot, or INNES plot from the "Mesopore distribution analysis" sub menu.



- Micropore distribution analysis
  Choose MP plot, HK plot, SF plot, or CY plot from the "Micropores distribution analysis" sub menu.



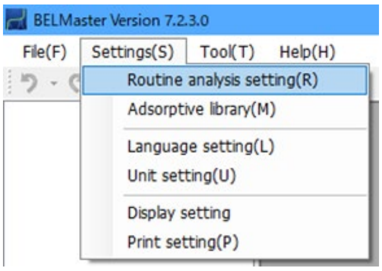
➢ Restart work

Select "File(F)" → "Restart work(W)" to restart operation by opening the file used before the analysis software was terminated.

➢ Quit

Select "File(F)" and then "Quit(Q)". The analysis software will end.

“Settings” menu



➢ Routine analysis setting

Specify the analysis methods to execute in a routine analysis.

→ Operation P.208 “How to use [Routine analysis]”

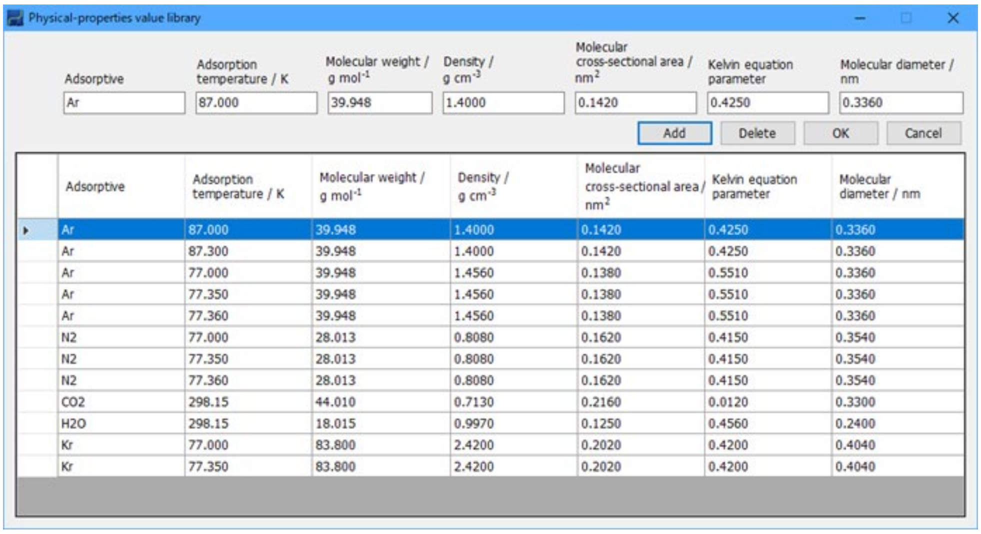
➢ Adsorptive library

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 software will execute an analysis based on this adsorption information. The default adsorptive information data is as follows.

Adsorptive	Adsorption temperature / K	Molecular weight / g mol^{-1}	Density / g cm^{-3}	Cross-sectional area / nm^2	Kelvin equation parameter	Molecular diameter / nm
Ar	77.000 77.350 77.355 77.360	39.948	1.4560[※1]	0.1380[※3]	0.5510	0.3360
Ar	87.000, 87.270 87.300	39.948	1.4000[※2]	0.1420[※3]	0.4250	0.3350
N_2	77.000 77.350 77.355 77.360	28.013	0.8080[※2]	0.1620[※7]	0.4150	0.3540
CO_2	298.15	44.010	0.7130[※4]	0.2160[※7]	0..0120	0.3300
H_2O	298.15	18.015	0.9970[※5]	0.1250[※7]	0.4560	0.2400
Kr	77.000 77.350 77.355 77.360	83.800	2.4200[※6]	0.2020[※7]	0.4200	0.4040

«Reference»

- ※1 *Carbon*, **25**, 69-75 (1987)
- ※2 ISO 15901-3
- ※3 ISO 18757
- ※4 National Institute of Standards and Technology, http://webbook.nist.gov/chemistry/fluid/
- ※5 Chemistry handbook basic 4th edition, Chemical Society of Japan, Maruzen Co., LTD.
- ※6 The properties of GASES & LIQUIDS, 4th edition, Robert C Reid, John M. Prausnitz, Bruce E. Polig.
- ※7 Sicence of adsorption 2nd edition, Seiichi KONDOU, Tatuo ISHIKAWA, Ikuo ABE, Maruzen Co., LTD.



Adsorptive	Adsorption temperature / K	Molecular weight / g mol^{-1}	Density / g cm^{-3}	Molecular cross-sectional area / nm^2	Kelvin equation parameter	Molecular diameter / nm
Ar	87.000	39.948	1.4000	0.1420	0.4250	0.3360

Adsorptive	Adsorption temperature / K	Molecular weight / g mol^{-1}	Density / g cm^{-3}	Molecular cross-sectional area / nm^2	Kelvin equation parameter	Molecular diameter / nm
Ar	87.000	39.948	1.4000	0.1420	0.4250	0.3360
Ar	87.300	39.948	1.4000	0.1420	0.4250	0.3360
Ar	77.000	39.948	1.4560	0.1380	0.5510	0.3360
Ar	77.350	39.948	1.4560	0.1380	0.5510	0.3360
Ar	77.360	39.948	1.4560	0.1380	0.5510	0.3360
N2	77.000	28.013	0.8080	0.1620	0.4150	0.3540
N2	77.350	28.013	0.8080	0.1620	0.4150	0.3540
N2	77.360	28.013	0.8080	0.1620	0.4150	0.3540
CO2	298.15	44.010	0.7130	0.2160	0.0120	0.3300
H2O	298.15	18.015	0.9970	0.1250	0.4560	0.2400
Kr	77.000	83.800	2.4200	0.2020	0.4200	0.4040
Kr	77.350	83.800	2.4200	0.2020	0.4200	0.4040

Adsorptive	Enter a name of adsorptive. If the input conforms to the adsorptive name and adsorption temperature of measurement data, the system automatically executes analysis by using the input parameters.
Adsorption temperature / K	Enter an adsorption temperature. If the input conforms to the adsorptive name and adsorption temperature of measurement data, the system automatically executes analysis by using the input parameters.
Molecular weight / g mol^{-1}	Set molecular weight of the adsorptive.
Density / g cm^{-3}	Set density of the adsorbate.
Molecular cross-sectional area / nm^2	Set a molecular cross-section area of the adsorbate.
Kelvin equation parameter	Set a Kelvin equation parameter specific to the adsorbate. The parameter is calculated from surface tension in liquid state γ (N m^{-1}), molar volume V_L (m^3 mol^{-1}), gas constant R (8.314 J K^{-1} mol^{-1}), and adsorption temperature T (K) by using the following equation: $\frac{2\gamma V_L}{2.303\,R\,T} \times 10^6$
Molecular diameter / nm	Set a molecular diameter of the adsorbate.

Add button	Used to save an additional combustion of input parameters in the library.
Delete button	Used to delete a selected combination of parameters from the library.
OK button	Used to close the physical property library setting window with adopting the setting change.
Cancel button	Used to close the physical property library setting window without adopting the setting change.

➢ Language setting

Select “Settings(S)” → “Language setting(L)” to change the language.

Select “English” or “XXX", and click the OK button.

“XXX” is displayed if a resource file which corresponds to the language of OS exists. If not, only “English” is displayed.

➢ Unit setting

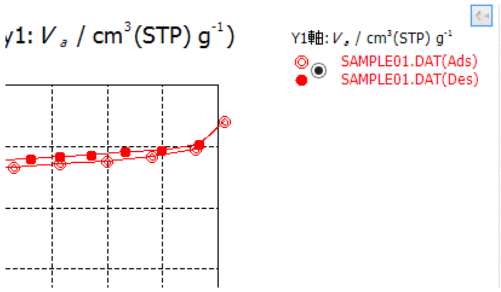
Select “Settings(S)” → “Unit setting(U)” to change the unit.

Select “nm” or “Å” for [Axial unit], and select “kPa” or “Torr” for [Pressure unit], and then click the OK button.

➢ Display setting

Select “Settings(S)” → “Display setting” to change the setting about the button for selecting data.
Select “Visible” or “Invisible” and then click the OK button.
In the case of “Visible”, the radio button is displayed on analysis window and selecting the analysis data is possible by them.

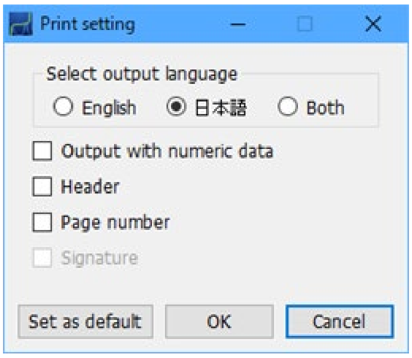
- The radio button may be overlayed on the analysis data due to the display size or aspect ratio.



➢ Print setting

Select “Settings(S)” → “Print setting(P)” to change print settings. The items checked will be printed with a graph. Select a desired output language, and click the OK button.

- If the Security software mode is not available, the checkbox of “signature” is not able to be selected.



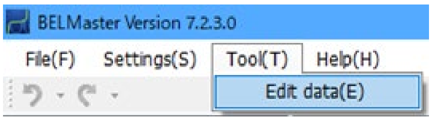
Select output language	Set a language to print. Select “English”, “XXX” or “Both”. “XXX” is displayed if a resource file which corresponds to the language of OS exists. If not, “English” and “Both” are displayed.
Output with numeric data	To output numeric data simultaneously during printing, check this checkbox.
Header	Used to insert a header at the top of the first page during printing. Save the header as “DefaultHeader.bmp” in the same folder as the execution file. Available print size is 700 × 45 pixels. If the dimension is not matched, it will be enlarged or reduced during printing.
Page number	Used to insert page numbers during printing.
Set as default button	A setting will be stored, even after the analysis software is closed.
OK button	Used to register a setting.
Cancel button	Pressing this button cancels a change, and closes the print setting window.

Tool menu

➢ Edit data

Select “Tool(T)” and “Edit data(E)”.
Then you can edit the settings used for the measurements (sample and measurement conditions).

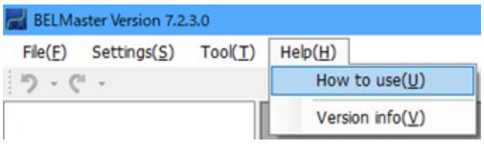
→ Operation P. 55 “Edit data”



“Help” menu

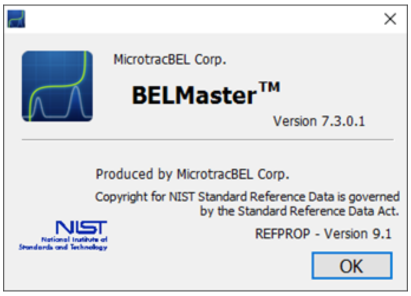
➢ How to use

Select “Help(H)” and “How to use(U)”.
The BELMaster manual can be refered here.



➢ Version info

Select “Help(H)” and “Version info(V)”.
You will find the version information here.



MicrotracBEL Corp.

BELMaster™

Version 7.3.0.1

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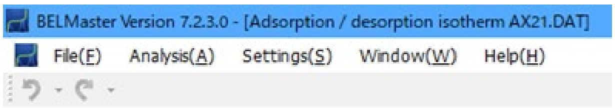
REFPROP - Version 9.1

Analysis window

Menu structure

While analyzing data (more than one data set is open), “Menu” window displays when the analysis window is actived.



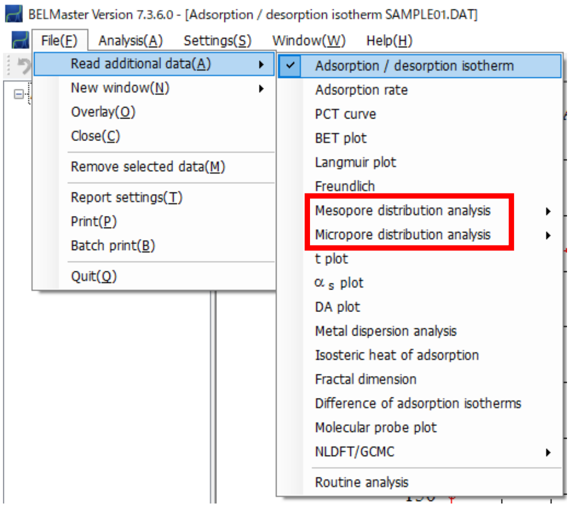
BELMaster Version 7.2.3.0 - [Adsorption / desorption isotherm AX21.DAT]

File	Analysis	Settings	Window	Help
Read additional data	Display numerical data	Data color settings	Cascade (Analysis window)	How to use
Adsorption / desorption isotherm	Adsorption / desorption isotherm	Analysis parameters settings		Vesion info
Adsorption rate	PCT curve	X-axis display settings	Tile Horizontally (Analysis window)	
PCT curve	BET plot	Y-axis display settings		
BET plot		Plot settings	Tile Verticaly (Analysis window)	
⋮		Smoothing settings		
⋮		Routine analysis settings	Cascade	
New window		Adsorptive library	Adsorptive library	
New window open			Tile vertically	
Adsorption / desorption isothem			Slide	
Adsorption rate				
PCT curve		Setting menu during Molecular probe analysis		
⋮				
⋮		Analysis setting		
Overlay		Edit data		
Close				
Remove selected data				
Report settings				
Print				
Batch print				
Quit				

“File” menu

➢ Read additional data

Select “File(F)” → “Read additional data(A)” → “(Analysis method)” to read additional data.
The data is displayed as another graph on the same analysis window graph in the case of reading additional data.



- Select DH plot, BJH plot, CI plot or INNES plot from the “Mesopore distribution analysis” sub menu.
- Select MP plot, HK plot, SF plot, or CY plot from the “Micropore distribution analysis” sub menu.

➢ New window

Select “File(F)” → “New window(N)” → “Open new window” to open an empty analysis window.

Also, select “File(F)” → “New window(N)” → “(Analysis method)” to open a new analysis window showing a graph using a selected analysis method.

→ Operation P.28 “Open file”

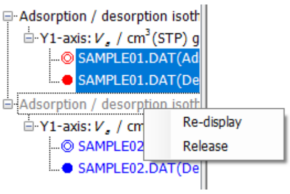
➢ Overlay

Select “File(F)” → “Overlay(O)” to display up to 10 pieces of data overlaid on a graph in the analysis window currently active.

→ Operation P.33 “Overlaying on active data (graph)“

➢ Close

Select “File(F)” → “Close(C)” to close the graph in the analysis window currently active.
Once the graph is closed, it becomes unable to be selected even from the left sub window.
To select the graph which is closed once, if “Re-display” is selected from the right click menu with the analysis data in the sub window selected, the data can be analyzed again.



➢ Remove selected data

Select “File(F)” → “Remove selected data(M)” to release all analysis data displayed in the graph in the analysis window currently active.

If “Remove selected data” is selected from the right click menu with the analysis data in the sub window selected, the analysis data can be released one by one.

➢ Report settings

An analysis report setting window will appear.

→ Operation P.210 "Output an analysis report"

- If Microsoft Excel® is not installed on your PC, this function cannot be used.

➢ Print

Select “File(F)” and “Print(P)”. Then you can print a data analysis graph of the active analysis window.

→ Operation P.51 “Printing analysis data”

➢ Batch print

Select “File(F)” and “Batch print(B)”. Then you can select multiple analysis data you want to print from the currently active analysis window and print the analysis data (graphs).

- Data in different analysis windows cannot be printed in a batch.

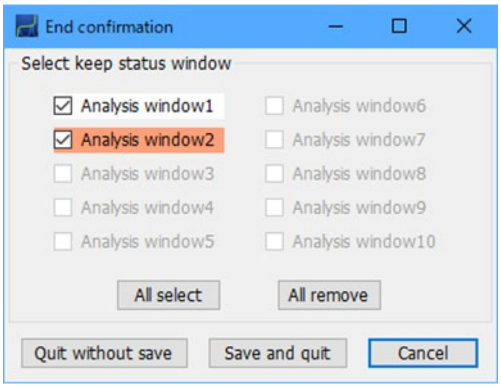
→ Operation P.53 ”Batch printing analysis data”

➢ Quit

Select “File(F)” and “Quit(Q)”. Then you can quit the analysis software.

Quitting from analysis window (in displaying multiple windows)

- Since the “End confirmation” window appears, select an analysis window to close after saving the state, and then click the Save and quit button.
- To quit without saving, click the Quit without save button.



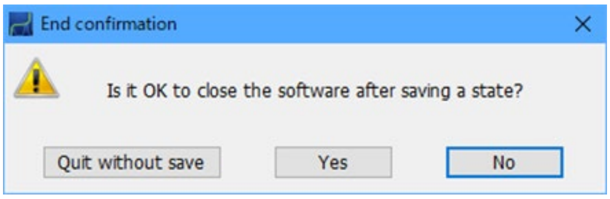
End confirmation

Select keep status window

☑ Analysis window1 ☐ Analysis window6
☑ Analysis window2 ☐ Analysis window7
☐ Analysis window3 ☐ Analysis window8
☐ Analysis window4 ☐ Analysis window9
☐ Analysis window5 ☐ Analysis window10

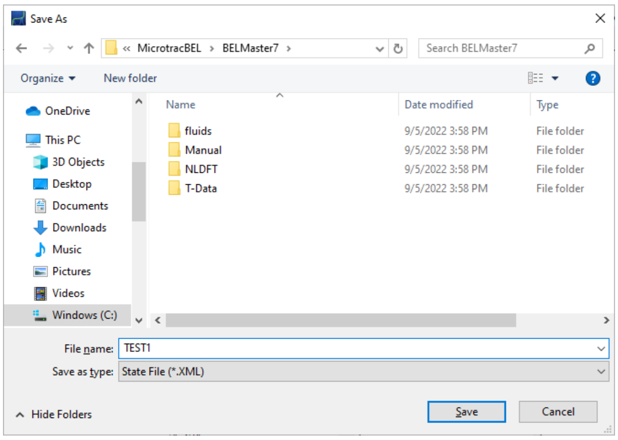
Quitting from analysis window (in displaying single window)

- Since the “End confirmation” window appears, click the YES button.
- To quit without saving, click the Quit without save button.



Is it OK to close the software after saving a state?

In the case of quitting after saving the state, input the state file name. From the next time onwards, you can select any of the saved state files to resume.



Name	Date modified	Type
fluids	9/5/2022 3:58 PM	File folder
Manual	9/5/2022 3:58 PM	File folder
NLDFT	9/5/2022 3:58 PM	File folder
T-Data	9/5/2022 3:58 PM	File folder

File name: TEST1
Save as type: State File (*.XML)

“Analysis” 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”, numerical data is displayed in the same analysis window.

It will display numerical data for the active data in the currently active window.

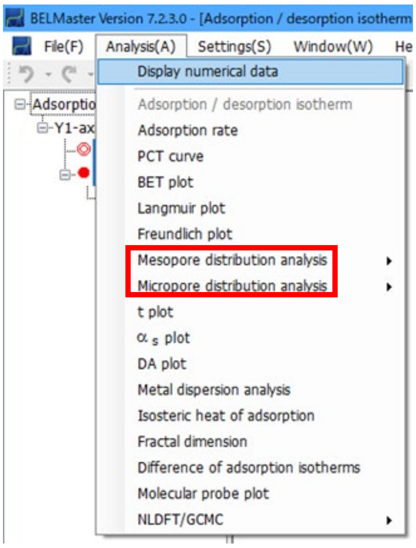
→ Operation P.35 ”Display the numerical values of data on the graph”

If you select “Analysis(A)” and then any analysis method with selecting active data, analysis result for active data is displayed in the same analysis window.
If you select “Analysis(A)” and then any analysis method with selecting Y1-axis or Y2-axis, analysis results for the all data included the graph are displayed in the same analysis window.

→ Operation P.28 ”Open file”

→ Analysis method P.69 "Adsorption/desorption isotherm"～

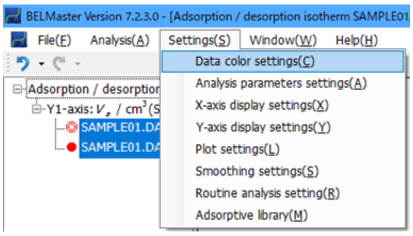
- Select DH plot, BJH plot, CI plot or INNES plot from the “Mesopore distribution analysis” sub window.
- Select MP plot, HK plot, SF plot, or CY plot from the “Micropore distribution analysis” sub menu.

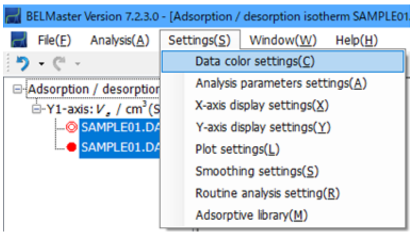


“Setting” menu

Select “Settings(S)” and then any of the items you want to set. A setting window will open and you can specify individual settings.

→ Operation P.37 "Setting change“





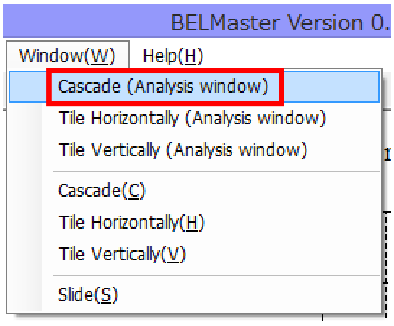
When executing a Molecular probe method analysis.

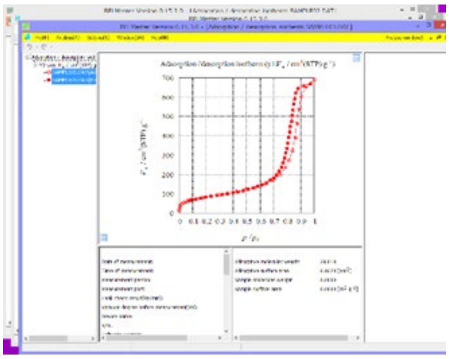
“Window” menu

A method can be selected to display multiple pieces of analysis data at the same time.

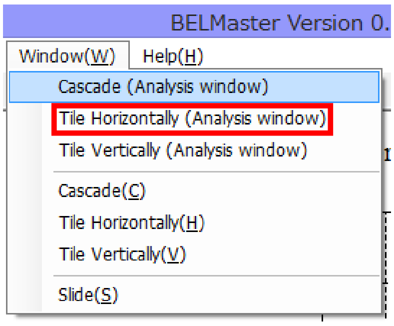
➢ When a method is selected to display analysis window that opened separately

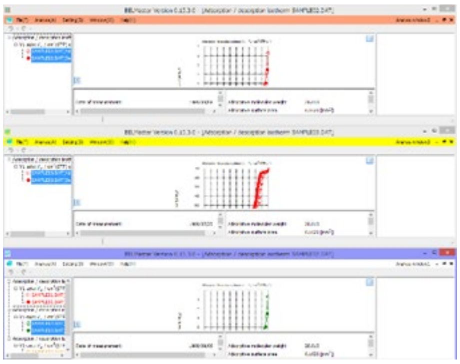
“Window (W)” → ”Cascade (Analysis window)“



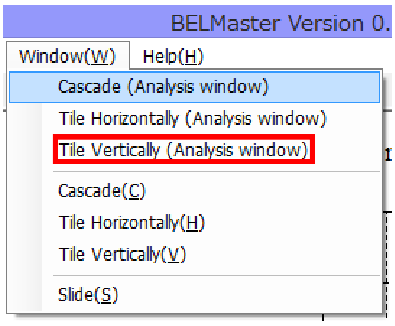


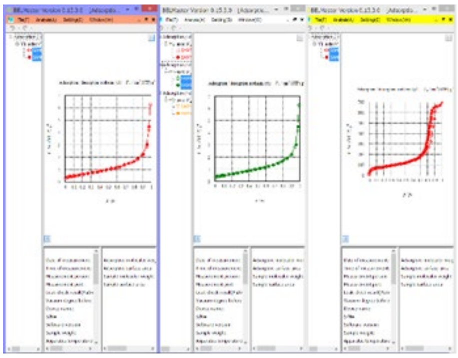
“Window (W)” → ”Tile Horizontally (Analysis window)”





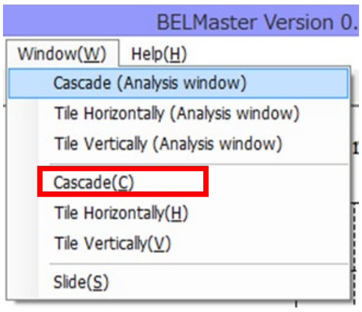
“Window (W)” → ”Tile Vertically (Analysis window)”

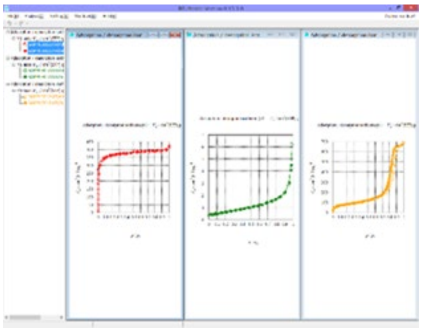




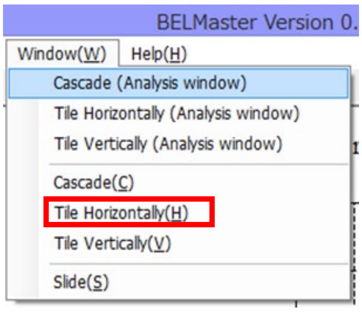
➢ When a method is selected to display an analysis window

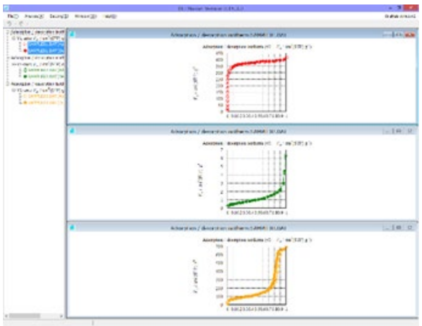
"Window (W)" → "Cascade (C)"



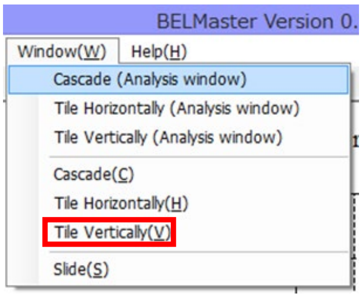


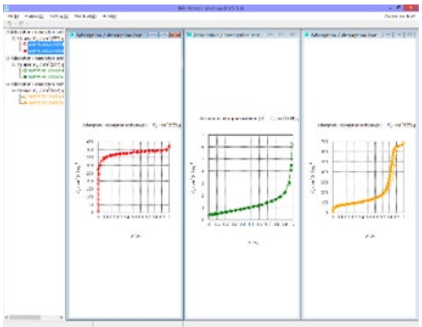
"Window (W)" → "Tile Horizontally (H)"



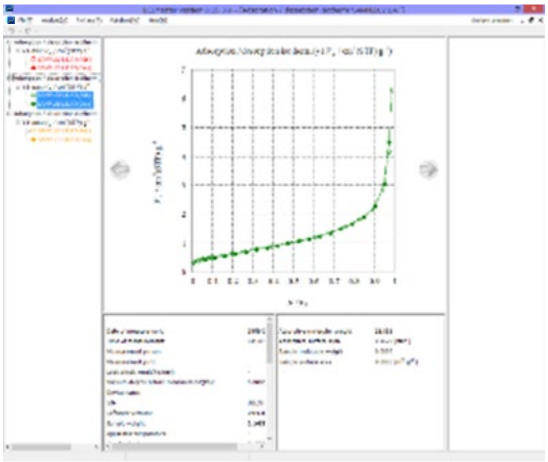


"Window (W)" → "Tile Vertically (V)"





➢ Slide

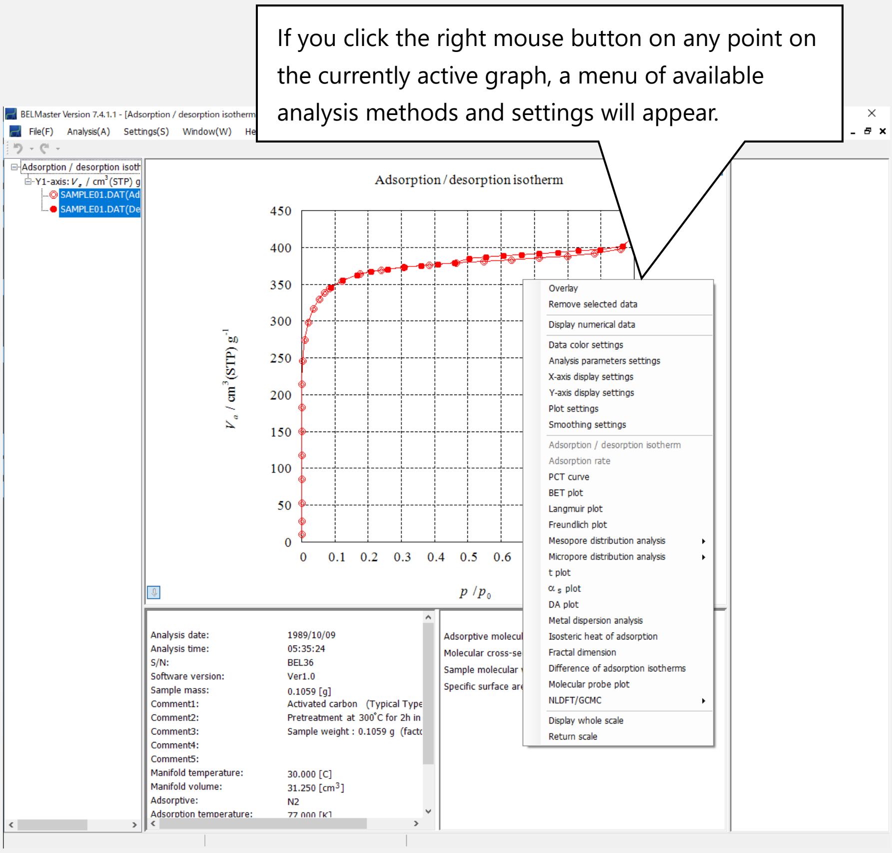


Select "Window(W)" → "Slide(S)" to turn on/off slide display.
If slide display is turned on, an arrow button appears each at the left and right edges of the graph drawing window. If the right-pointing arrow button is pressed, the next lower analysis data becomes active in the left sub window. If the left-pointing arrow button is pressed, the next upper analysis data becomes active in the left sub window.
If the slide display is turned off, the arrow buttons disappear from the left and right edges of the graph drawing window.

"Help" menu

→ For details P.17 ""Help" menu"

Right click menu



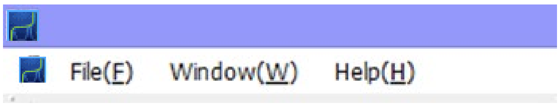
If you click the right mouse button on any point on the currently active graph, a menu of available analysis methods and settings will appear.

Analysis date: 1989/10/09
Analysis time: 05:35:24
S/N: BEL36
Software version: Ver1.0
Sample mass: 0.1059 [g]
Comment1: Activated carbon (Typical Type
Comment2: Pretreatment at 300°C for 2h in
Comment3: Sample weight : 0.1059 g (facto
Comment4:
Comment5:
Manifold temperature: 30.000 [C]
Manifold volume: 31.250 [cm^3]
Adsorptive: N2
Adsorption temperature: 77.000 [K]

Data window

Menu structure

The menu that appears after opening the analysis window and selecting [Display numerical data] from the “Analysis(A)” menu.



File	Window	Help
Print	Cascade (Analysis window)	How to use
Save csv file	Tile Horizontally (Analysis window)	Version info
Save aif file*	Tile Vertically (Analysis window)	
Delete	Cascade	
	Tile Horizontally	
	Tile Vertically	
	Slide	

*: “Save aif file” is displayed only when the numerical data of adsorption / desorption isotherm is being displayed.

“File” menu

➢ Print

Select “File(F)” and then “Print(P)”. You can print the numerical data from the active data window.

→ Operation P.51 “Printing analysis data”

➢ Save csv file

Select “File(F)” and then “Save csv file(C)”. You can save the numerical data from the currently active data window.

→ Operation P.49 “Save analysis data”

➢ Save aif file

Select “File(F)” and then “Save aif file”. You can save the measurement data as aif file format from the currently active data window.

→ Operation P.50 “Conversion of measurement data to AIF file”

➢ Delete

Select “File(F)” and then “Delete(D)”. The currently active data window (numerical data) will close.

“Window” menu

A method can be selected to display multiple pieces of analysis data at the same time.

- The slide display can not be displayed with a numeric data.

→ For details P.23 ““Window” menu”

“Help” menu

→ For details P.17 ““Help” menu”

Reading in analysis data

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

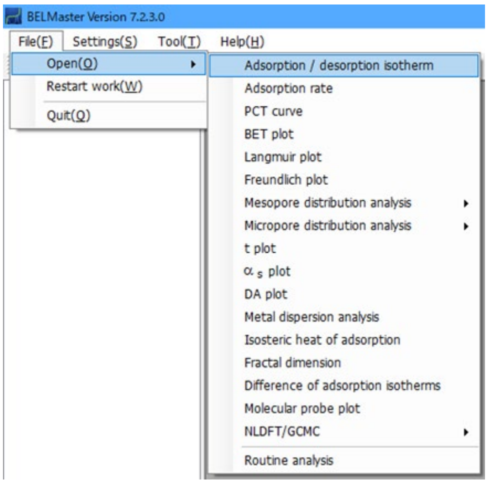
Open file

There are 3 methods: the first is to open a new analysis window, the second is to read the data as another analysis data in the same analysis window, and the third is to overlay new analysis data on the analysis data already open.

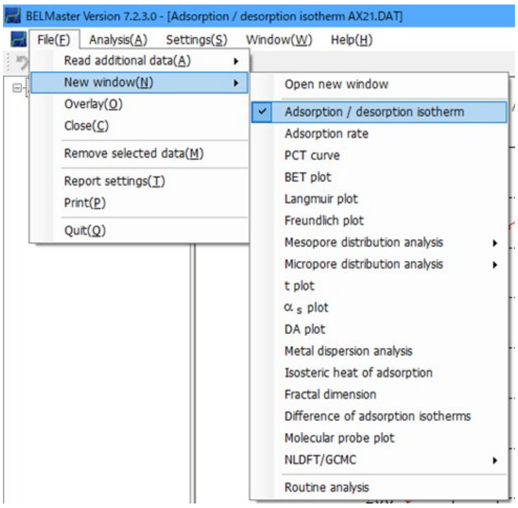
Method to open a new analysis window

To open a file from the main window, open the data analysis window by selecting “File(F)”. Then select “Open(O)” and choose an analysis method. The graphic data analysis window will be displayed.

- Analysis methods on the menu that are grayed out cannot be selected.

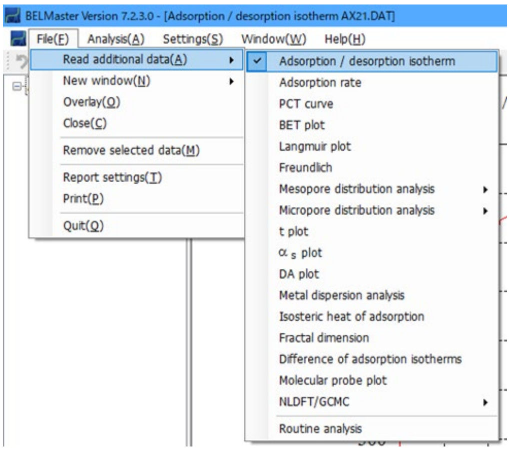


To open a file with an analysis window open, open a new analysis window showing a graph drawn in the analysis method specified by selecting “File(F)” → “New window(N)” → “(Analysis method)”.
If you select “File(F)” → “New window(N)” → “Open new window”, the software opens a new analysis window (blank).



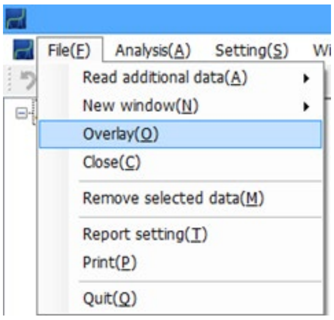
Method to read as different analysis data in the same analysis window

With an analysis window open, read additional data by selecting “File(F)” → “Read additional data(A)” → “(Analysis method)”.



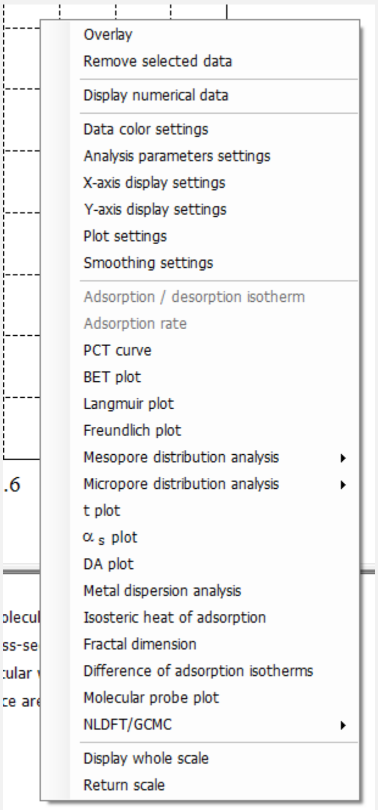
Method to overlay new analysis data on the analysis data already opened

Select “File(F)” and then “Overlay(O)” on the analysis window menu.

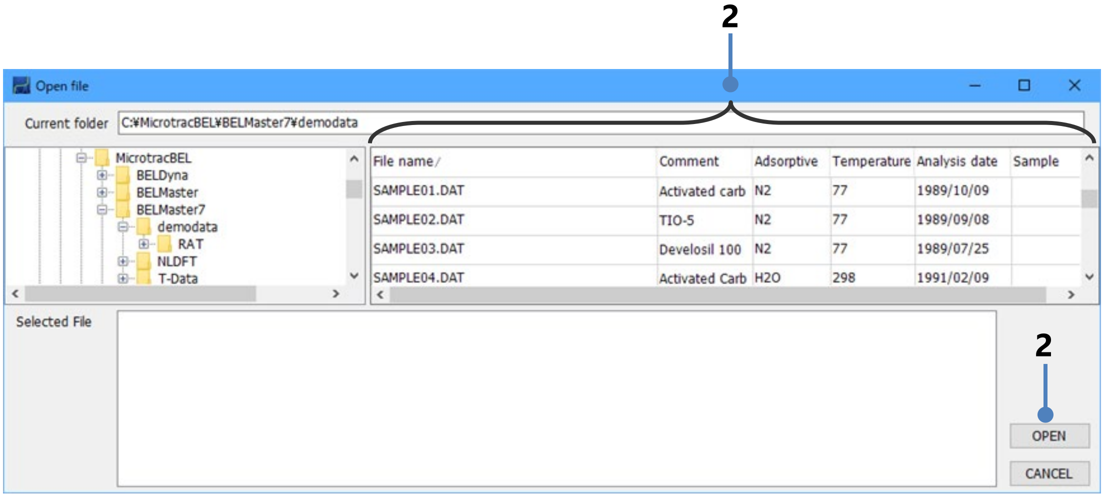


Right click menu

It is also possible to select “Overlay” from the menu displayed by right clicking the mouse on a graph.



1 If attempt is made to open a file in one of the methods, the “Open file” window shown below will appear.



Current folder: C:¥MicrotracBEL¥BELMaster7¥demodata

File name	Comment	Adsorptive	Temperature	Analysis date	Sample
SAMPLE01.DAT	Activated carb	N2	77	1989/10/09	
SAMPLE02.DAT	TIO-5	N2	77	1989/09/08	
SAMPLE03.DAT	Develosil 100	N2	77	1989/07/25	
SAMPLE04.DAT	Activated Carb	H2O	298	1991/02/09	

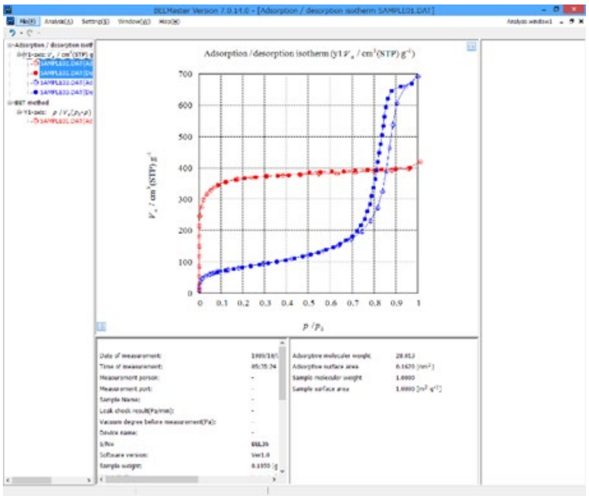
2 Select the data file you want to analyze, and click the OPEN button. The software will read in the selected file.

- Open multiple data files by holding down the Ctrl key and clicking on the various files you want.
- 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”.

  The software 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.
- “Sample” is displayed only for .NDAT file.

3 The software will analyze the data using the selected analysis method and display a data analysis graph.

- The figure on the right is an example of an adsorption/desorption isotherm.

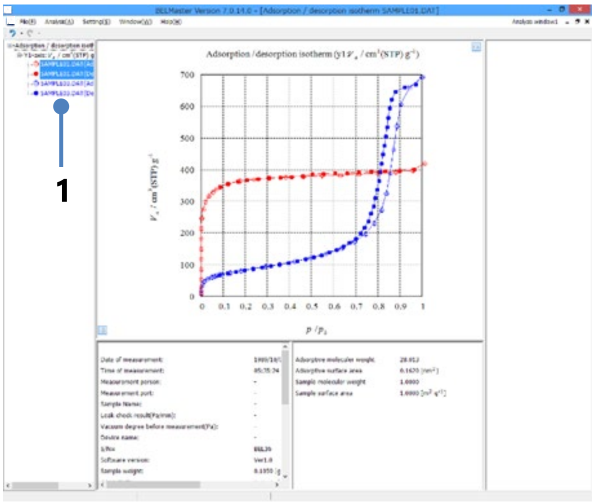


Analysis of active data (graph)

The data having been analyzed can also be analyzed differently.

1 Select the data you want to analyze.

- When data is overlaid, select the data you want to analyze from the left sub window.



There are two ways after this.

- Select from the analysis window menu

→ Please proceed to Step **2**.

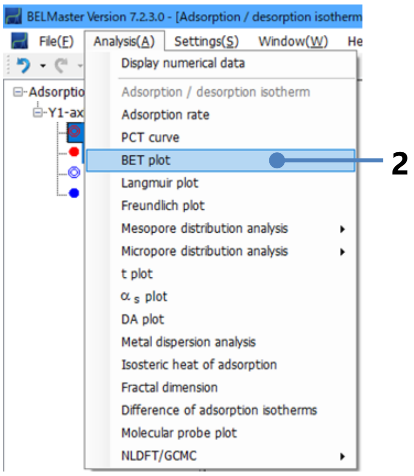
- Click the right mouse button on the graph and select from the menu that pops up

→ Please proceed to Step **4**.

Select from the analysis window menu

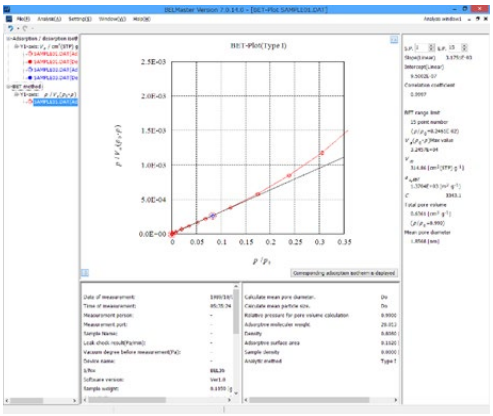
1 Select “Analysis(A)” and then an analysis method from the “Analysis” method menu.

Select “Analysis(A)” and then an analysis method from the “Analysis” method menu with selecting “Y1-axis: ” or “Y2-axis: ” (not only an active data), the all data involved are analyzed at the same time by the selected analysis method.



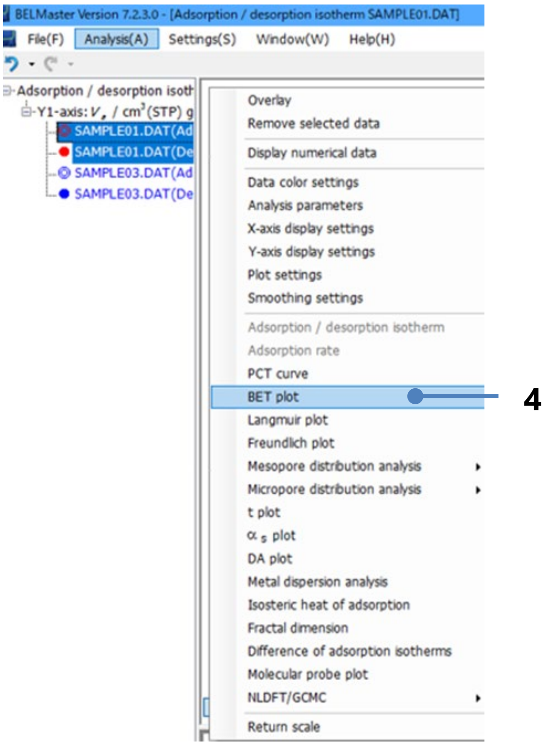
2 A new data analysis window will be opened, and a graph of the specified analysis will be displayed.

- The figure on the right is an example of a “BET plot”.



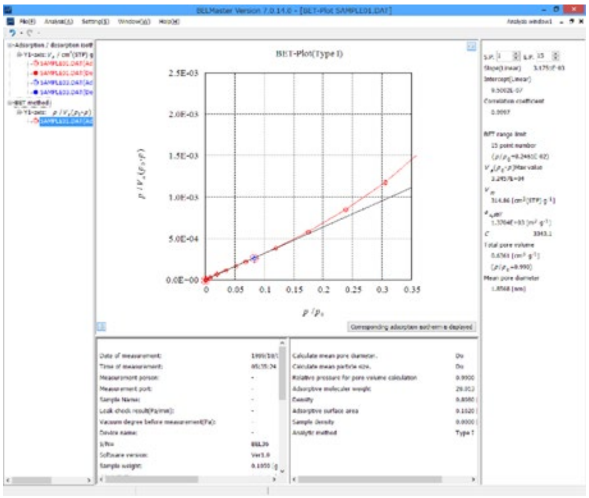
Click the right mouse button on the graph and select from the menu that pops up

3 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".



Overlaying on active data (graph)

You can add another data analysis curve to the current analysis graph window. The curves will be overlapped.

Maximum number of pieces of data that can be overlaid is as follows:

(The number is possible to be restricted to smaller than below due to analyze both adsorption / desorption branch.)

• An isosteric heat of adsorption	: 3 data sets per graph
• Molecular probe method	: 1 data set per graph
• NLDFT/GCMC method	: 5 data sets per graph
• Adsorption/desorption isotherm and analysis methods other than those above	: 10 data sets per graph

1 Click to activate the analysis window of a graph on which data is overlaid.

There are three ways after this.

・Select from the analysis window menu

→ Please proceed to Step **2**.

・Click the right mouse button on the graph and select from the menu that pops up

→ Please proceed to Step **4**.

・Drag and drop

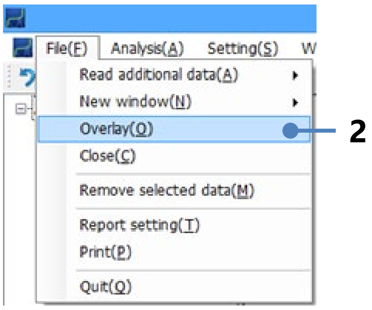
→ Please proceed to Step **6.**

Select from the analysis window menu

2 Select "File(F)" and then "Overlay(O)" on the analysis window menu. The "Open file" window will appear. Select a file.

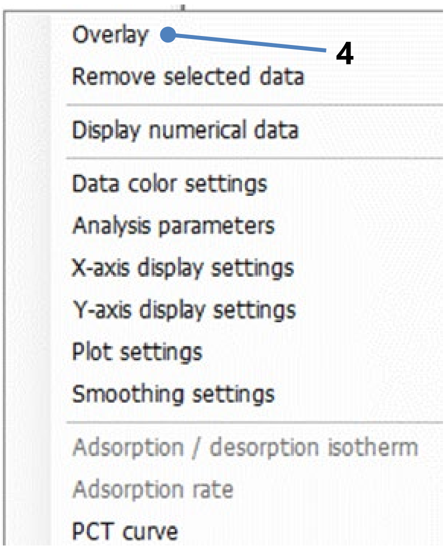
After analyzing data using a specified analysis method, the software displays this data overlapped on the graph.

→ How to select a file P.28 "Open file"



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

Click the right mouse button on the graph and select from the menu that pops up



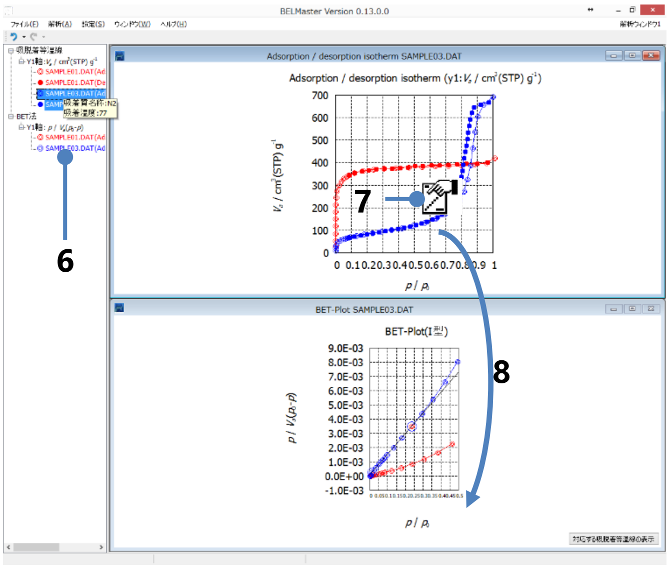
4 The cursor on the graph and click the right mouse button. You can select "Overlay(O)" from the pop-up menu. The "Open file" window will appear. Select the data file from it.

→ How to select a file P.28 "Open file"

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

Drag and drop

It is possible to overlay data on a graph by drag-and-drop from other analysis data.



6 Select data to be overlaid on another analysis graph.

If more than two data sets are drawn on a window, click the data to be selected.

- In this case, multiple pieces of data cannot be selected.

7 If drag-and-drop is enabled for selected data, dragging on the data displays an icon.

8 With the icon displayed, drag-and-drop the data onto the analysis graph to which the data is to be added.

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

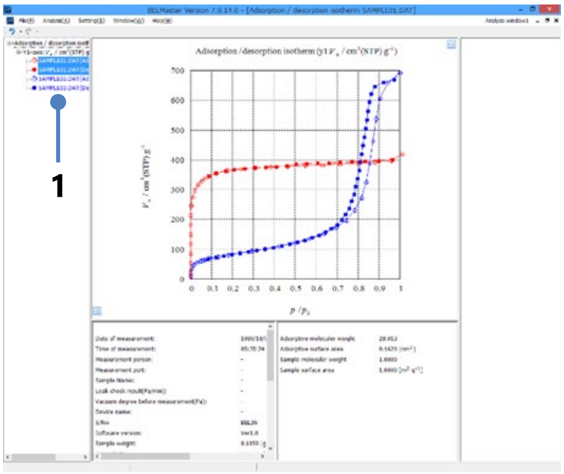
- The files on the desktop and folders can be overlaid by drag-and-drop.

Display the numerical values of data on the graph

1 Select data that you want to display numerical data from the left sub window.

If more than two data sets are drawn on a window, click the data to be selected.

- In this case, multiple pieces of data cannot be selected.



There are two ways after this.

・Select the data set from the analysis window menu

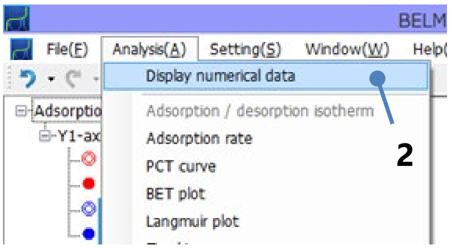
→ Please proceed to Step **2**.

・Select the data from the menu that pops up when you click the right mouse button

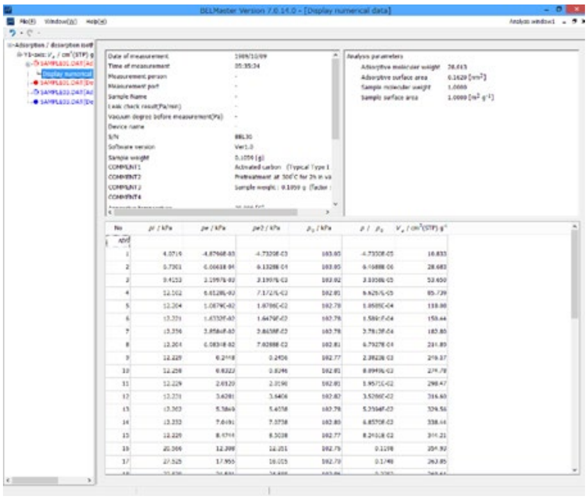
→ Please proceed to Step **4**.

Select the data set from the analysis window menu

2 Select “Analysis(A)” and then “Display numerical data” from the analysis window menu.

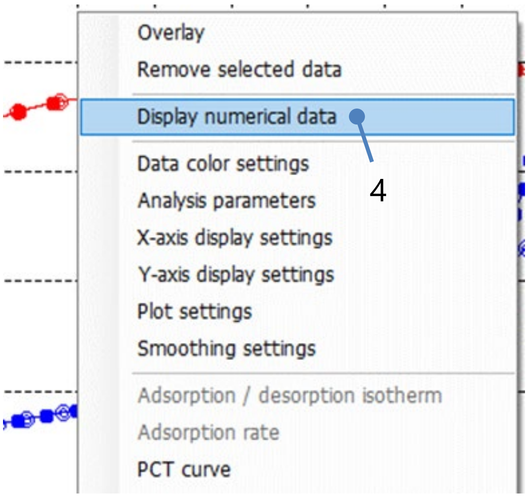


3 A new data window will open and display the numerical data from the specified data analysis.

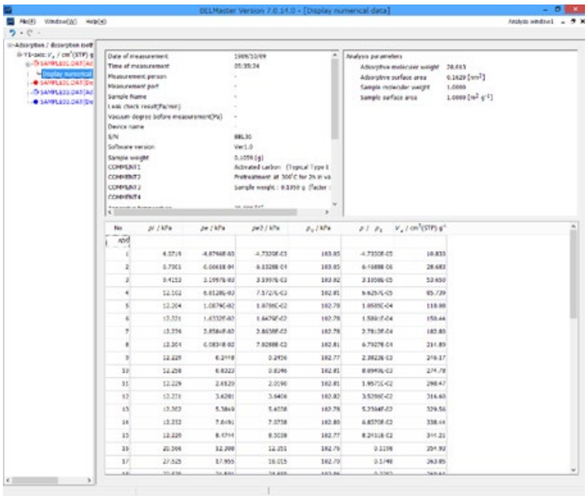


Select the data from the menu that pops up when you click the right mouse button

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 window will open and display the numerical data from the specified data analysis.



Setting change

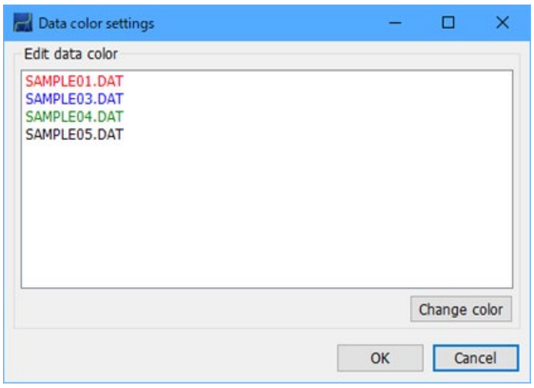
This chapter describes various parameter settings used for the analysis, graphic display and printing. Two methods can be used to display the "Settings" window.

- 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 the Set as default button, the current settings will be stored as the default settings. Default settings are created for each type of analysis.

Data color settings

The color of data can be changed. Select data with a color you want to change, and click the Change button to change the color as desired. After completing all data color settings, click the OK button to make the setting enable.

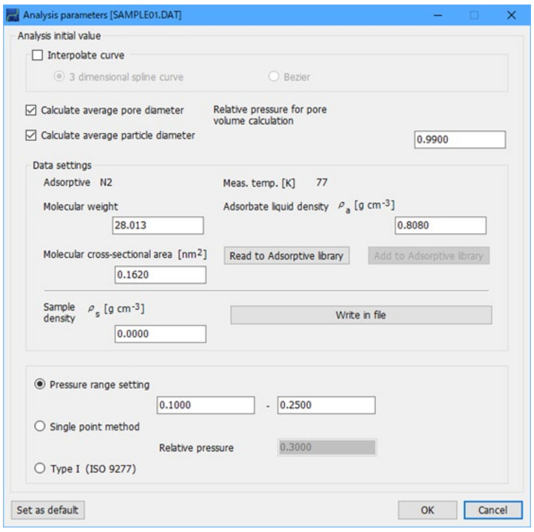


SAMPLE01.DAT
SAMPLE03.DAT
SAMPLE04.DAT
SAMPLE05.DAT

Analysis parameters setting

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".

For details, see the operation description form each analysis type.



☐ Interpolate curve
● 3 dimensional spline curve
○ Bezier
☑ Calculate average pore diameter
☑ Calculate average particle diameter
Relative pressure for pore volume calculation: 0.9900
Adsorptive: N2
Meas. temp. [K]: 77
Molecular weight: 28.013
Adsorbate liquid density ρ_a [g cm^{-3}]: 0.8080
Molecular cross-sectional area [nm^2]: 0.1620
Sample density ρ_s [g cm^{-3}]: 0.0000
● Pressure range setting: 0.1000 - 0.2500
○ Single point method
Relative pressure: 0.3000
○ Type I (ISO 9277)

Analysis initial value

➢ 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 "3 dimensional spline curve".
Bezier curve	Click the "Interpolate curve", and then click the "Bezier curve".

➢ Data settings

The density and adsorptive 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.

Molecular weight	Enter the molecular weight of the adsorptive
Adsorptive liquid density	Enter the density (g cm^{-3}) of the adsorptive
Sample molecular weight	Enter the molecular weight of the samples.
Sample density	Enter the density of the sample (g cm^{-3}).
Specific surface area	Enter the specific area of the sample (m^2 g^{-1}).
Kelvin equation parameter	Parameter specific to adsorbate To be calculated from surface tension in liquid sate γ (N m^{-1}), molar volume V_L (m^3 mol^{-1}), gas constant R (8.314 J K^{-1} mol^{-1}), and adsorption temperature T (K). $\frac{2\gamma V_L}{2.303\ R\ T} \times 10^6$
Add to adosorptive library button	If there is no record with the same adsorptive name and adsorption temperature in the physical property library, new molecular weight, adsorbate density, and Kelvin equation parameter value can be added to the adsorptive library. To change or delete adsorptive information that has already been recorded, select "Settings(S)" and then "Adsorptive library(M)". → P.13 ""Settings" menu"

t interpolation

➢ Data interpolation method

The method for file data interpolation can be selected from 3 methods [Linear], [Spline], and [Bezier].

➢ Specifying pore diameter / radius

To specify a pore diameter / range, check [Pore diameter range of the user setting] or [Pore radius range of the user setting] and enter a pore diameter / radius in numeric value. When the range is set, the ratio of whole pore volume to the pore volume in the range is calculated automatically

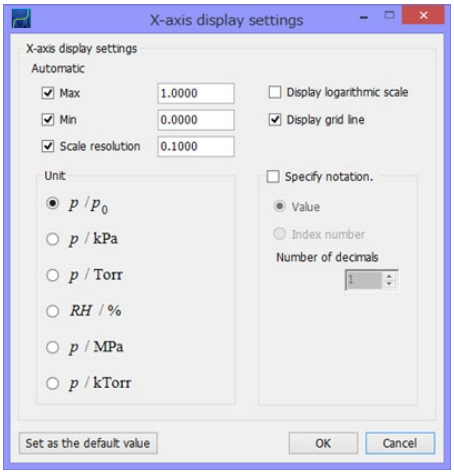
X-axis display settings

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 default button, and the currently set values will become the default for that analysis.

- Right figure is "X-axis display settings" window for Adsorption / desorption isotherm.



X-axis display settings

Automatic

☑ Max 1.0000

☑ Min 0.0000

☑ Scale resolution 0.1000

☐ Display logarithmic scale

☑ Display grid line

Unit

● p / p_0

○ p / kPa

○ p / Torr

○ RH / %

○ p / MPa

○ p / kTorr

☐ Specify notation.

● Value

○ Index number

Number of decimals 1

➢ Automatic

As to the Max, Min, and Scale resolution of X axis, uncheck the items to be set manually and enter numeric values. Check the items if to be set automatically.

If [Display logarithmic scale] is checked, a logarithmic scale is displayed on the graph, so that the scale resolution can no longer be set manually. It is also impossible to set maximum and minimum values to 0 and negative values.

If [Display grid line] is checked, grid lines are displayed on the graph.

➢ Unit

The unit of X-axis can be selected. Selectable unit varies depending on analysis.

➢ Notation

If [Specify notation] is checked, value or index can be specified for display of X-axis and the number of decimal places can be specified. If unchecked, the notation is automatically specified.

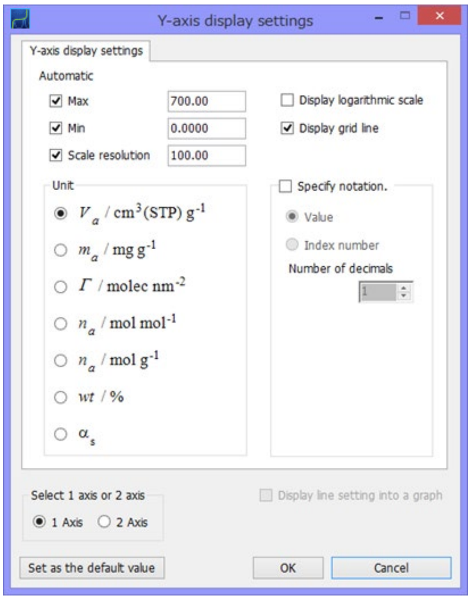
Y-axis display settings

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 default button, and the currently set values will become the default for that analysis.

- Right figure is "Y-axis display settings" window for Adsorption / desorption isotherm.



Y-axis display settings

Automatic

☑ Max 700.00

☑ Min 0.0000

☑ Scale resolution 100.00

☐ Display logarithmic scale

☑ Display grid line

Unit

● V_a / cm^3(STP) g^{-1}

○ m_a / mg g^{-1}

○ Γ / molec nm^{-2}

○ n_a / mol mol^{-1}

○ n_a / mol g^{-1}

○ wt / %

○ α_s

☐ Specify notation.

● Value

○ Index number

Number of decimals 1

Select 1 axis or 2 axis

● 1 Axis ○ 2 Axis

☐ Display line setting into a graph

➢ Automatic

As to the Max, Min, and Scale resolution of Y axis, uncheck the items to be set manually and enter numeric values. Check the items if to be set automatically.

If [Display logarithmic scale] is checked, a logarithmic scale is displayed on the graph, so that the scale resolution can no longer be set manually. It is also impossible to set maximum and minimum values to 0 and negative values.

If [Display grid line] is checked, grid lines are displayed on the graph.

➢ Unit

The unit of Y-axis can be selected. Selectable unit varies depending on analysis.

➢ Notation

If [Specify notation] is checked, value or index can be specified for display of Y-axis and the number of decimal places can be specified. If unchecked, the notation is automatically specified.

➢ Select 1 axis or 2 axis

1-axis and 2-axis types are selectable for Y axis. If [2 Axis] is selected, "Y2 axis" tab appears to enable settings for Y2 axis as well as for Y1 axis.

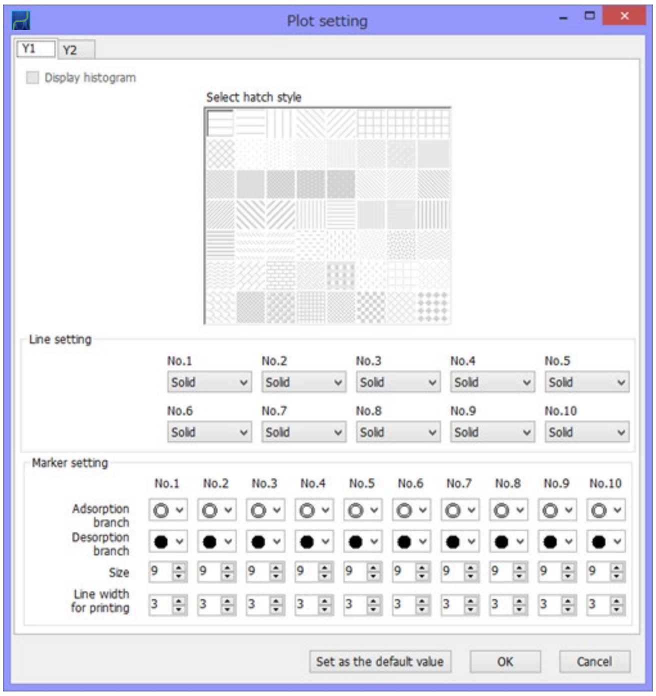
If [Display line setting into a graph] is checked, a legend for line types is displayed at the upper right of the graph.

Plot settings

The "Plot settings" window enables you to specify the types of lines to draw graph and markers, and to select whether to display graph as histogram by Y axis.

The settings can be saved if the Set as default button is pressed.

- Even when 2-axis type is selected for Y axis, only 1 axis can be shown in histogram.
- You cannot specify the "Plot settings" with the "Molecular probe method".
  However, you can do so in the "Analysis parameters settings".



Line setting

No.1	No.2	No.3	No.4	No.5
Solid	Solid	Solid	Solid	Solid

No.6	No.7	No.8	No.9	No.10
Solid	Solid	Solid	Solid	Solid

Marker setting

	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9	No.10
Adsorption branch	○	○	○	○	○	○	○	○	○	○
Desorption branch	●	●	●	●	●	●	●	●	●	●
Size	9	9	9	9	9	9	9	9	9	9
Line width for printing	3	3	3	3	3	3	3	3	3	3

➢ Line setting

Line types for No. 1 (1st read data) to No. 10 data can be specified.

- If [Display histogram] is checked, the line types cannot be specified.
  Select desired line types from [Select hatch style].

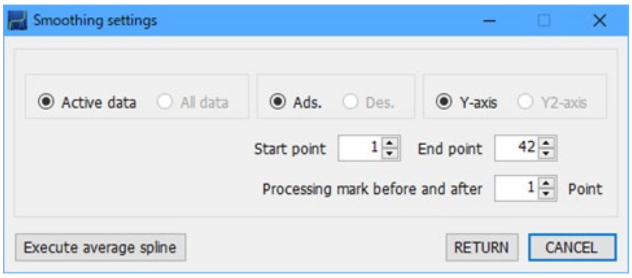
➢ Marker setting

Marker type, size, and line thickness for printing can be specified. Marker types can be specified for adsorption side and desorption side separately.

- If [Display histogram] is checked, marker settings are disabled.
  Select desired line types from [Select hatch style].

Smoothing settings

The “Smoothing settings” window enables you to change the smoothing settings and perform processing.



● Active data ○ All data
● Ads. ○ Des.
● Y-axis ○ Y2-axis
Start point 1 End point 42
Processing mark before and after 1 Point

After selecting whether to smooth only [Active Data] or [All data], and specifying smoothing start point and end point, and the number of processing points; you can smooth analysis data by clicking the Execute average spline button.

- If selected analysis data is Adsorption/desorption isotherm, only [Active Data] can be selected. In this case, [Ads.] or [Des.] needs to be selected. In the case Y2-axis is displayed, [Y-axis] or [Y2-axis] needs to be selected.

Clicking the RETURN button restores data before smoothing processing, and clicking the CANCEL button cancels smoothing processing and closes “Smoothing settings” window.

Display whole scale

By right-clicking on the graph, you can select "Display whole scale”.
Selecting [Display whole scale] will change the display range so that the entire data is shown without changing the units or linear/logarithmic settings. (The same range is displayed as when “Automatic” is selected for the X-axis or Y-axis settings.)

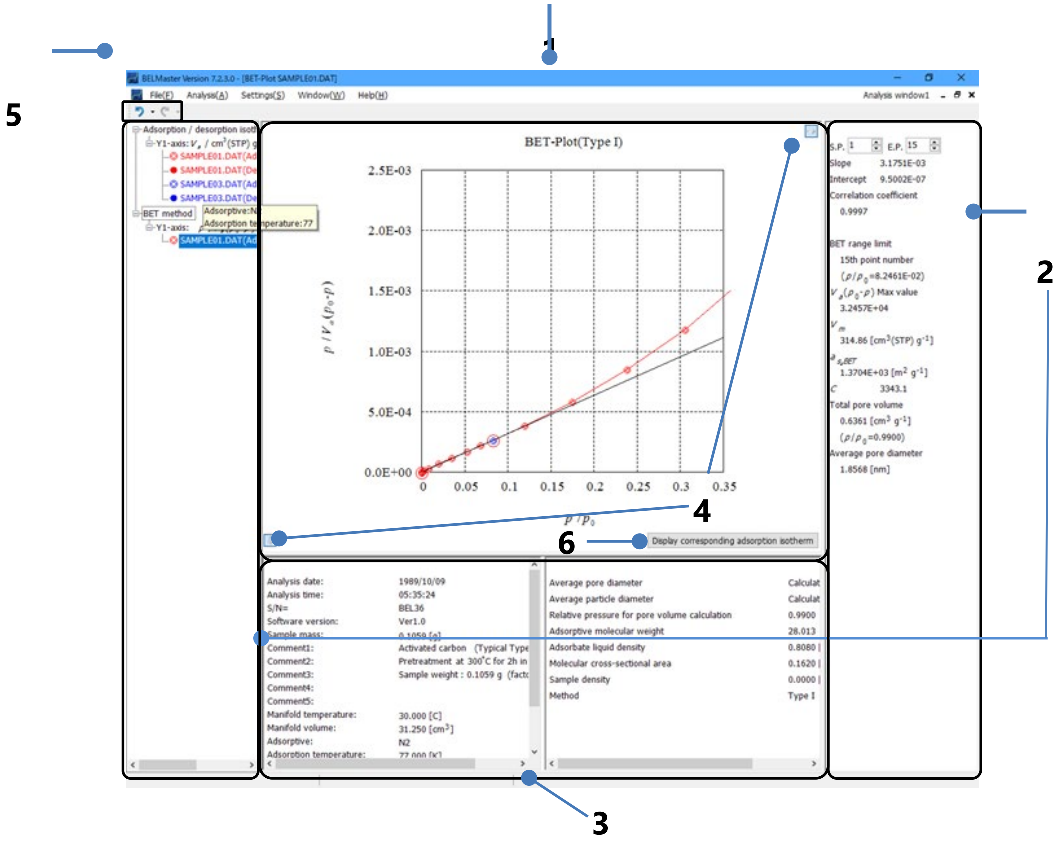
Return scale

By right-clicking on the graph, you can select "Return scale”.
Selecting [Return scale] will return the X-axis and Y-axis settings to their default values.

Analysis window

This chapter describes the operations common to the analysis window. For details about operations specific to each analysis method, see “Adsorption/desorption isotherm” to “Output an analysis report” (P. 69 to P. 210)

Operation of analysis window



S.P. 1 E.P. 15

Slope 3.1751E-03

Intercept 9.5002E-07

Correlation coefficient 0.9997

BET range limit
15th point number
$(p/p_0 = 8.2461E{-}02)$

$V_a(p_0 - p)$ Max value
3.2457E+04

V_m
314.86 [cm^3(STP) g^{-1}]

$a_{s,BET}$
1.3704E+03 [m^2 g^{-1}]

C 3343.1

Total pore volume
0.6361 [cm^3 g^{-1}]
$(p/p_0 = 0.9900)$

Average pore diameter
1.8568 [nm]

Analysis date:	1989/10/09
Analysis time:	05:35:24
S/N=	BEL36
Software version:	Ver1.0
Sample mass:	0.1059 [g]
Comment1:	Activated carbon (Typical Type
Comment2:	Pretreatment at 300°C for 2h in
Comment3:	Sample weight : 0.1059 g (fact
Comment4:	
Comment5:	
Manifold temperature:	30.000 [C]
Manifold volume:	31.250 [cm^3]
Adsorptive:	N2
Adsorption temperature:	77.000 [K]

Average pore diameter	Calculat
Average particle diameter	Calculat
Relative pressure for pore volume calculation	0.9900
Adsorptive molecular weight	28.013
Adsorbate liquid density	0.8080
Molecular cross-sectional area	0.1620
Sample density	0.0000
Method	Type I

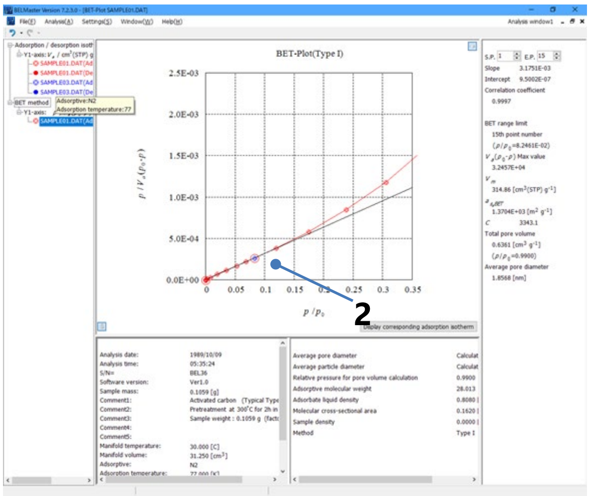
1	**Graph drawing window**	The window displayed at the center of the window is called graph drawing window.
2	**Sub window**	The windows displayed on the left and right sides of the graph drawing window are called sub windows. The window at the left is called left window, and the window displayed at the right is called right window.
3	**Slide sub window**	Basic information and analysis condition on active data are displayed.
4	⇩ ⇨ **button**	Clicking the buttons widens the graph drawing window. Clicking the buttons again restores original width.
5	**Back button,** **Next button**	Clicking the buttons performs Undo and Redo. Up to 10 times of operation can be performed.
6	**Display corresponding adsorption isotherm button**	Pressing this button displays adsorption / desorption isotherm in the range of analysis. → P.48 "Displaying corresponding adsorption isotherm”

Displaying 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.

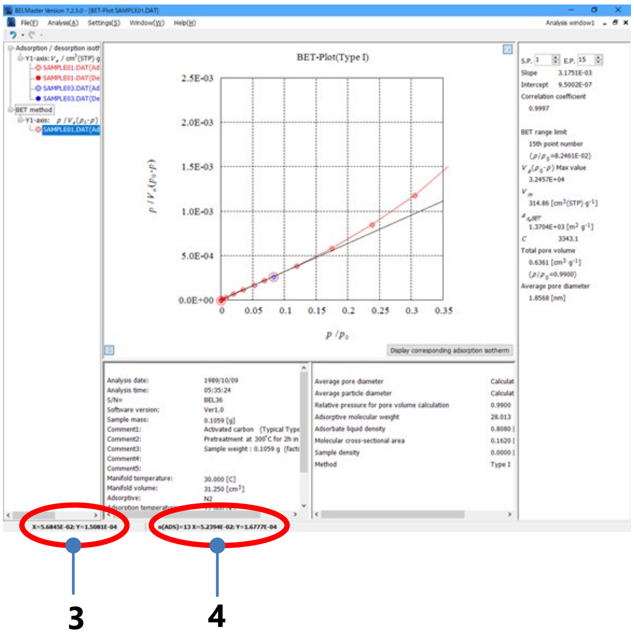
2 Move the pointer to the plot data set whose coordinate values you want to display, and click the left mouse button while pressing the Alt key.



3 The coordinates of the position you clicked on are shown on the left of the status bar (bottom bar on the window).

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.

- Drag-and-drop with Ctrl key held down enlarges the area.



```
X=5.6845E-02: Y=1.5081E-04
n(ADS)=13 X=5.2394E-02: Y=1.6777E-04
```

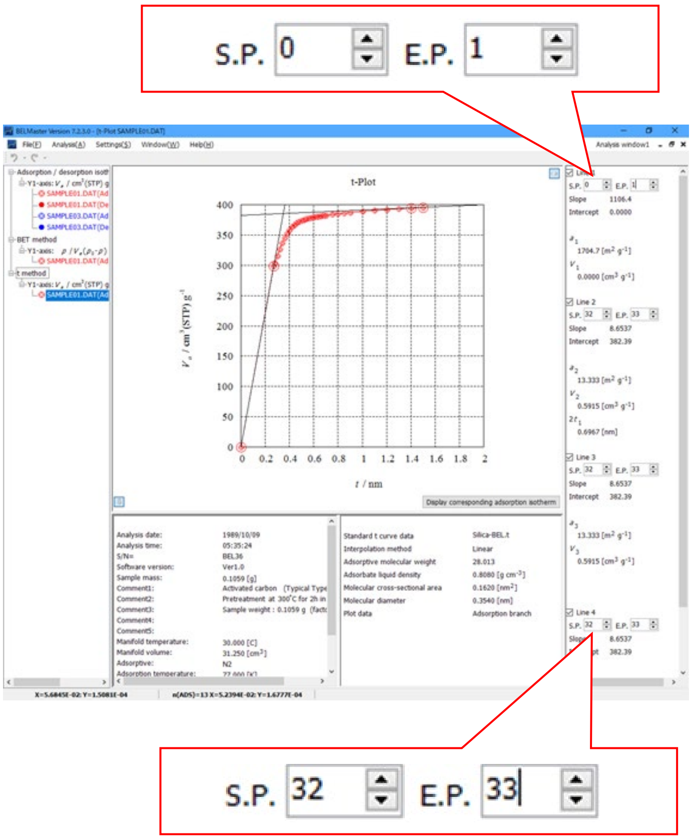
Setting of start and end points for linear regression

1 When analyses use the linear regression function (e.g. BET plot, Langmuir plot, Freundlich plot, *t* plot, α_s plot, DA plot, and metal dispersion analysis), boxes will appear on the right of the graph to let you enter start and end points.

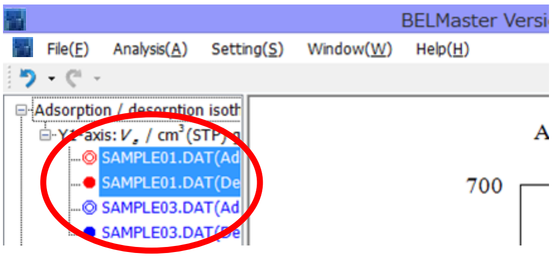
2 By changing these values, you can change the objective linear regression range.

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.



Displaying sub window



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

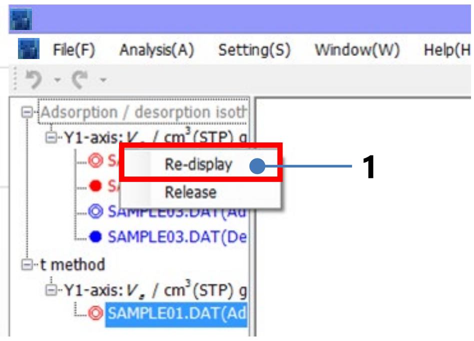
Even after graph data is deleted from the graph drawing window, the analysis method and file name will be retained.

- If you execute "Delete", the analysis method and file name on the left subwindow will be deleted.

To re-display a graph

Activate the "analysis method" for the data to be re-displayed on the sub window (it will be displayed in blue), and click the mouse right button to show the window indicated as 1.

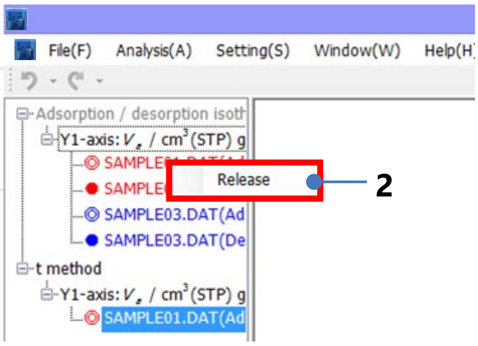
If you select "Re-display", the relevant graph will be re-displayed.



To release a graph

Activate the "analysis method" for the data to be destroyed on the sub window (it will be displayed in blue), and click the mouse right button to show the window indicated as 2.

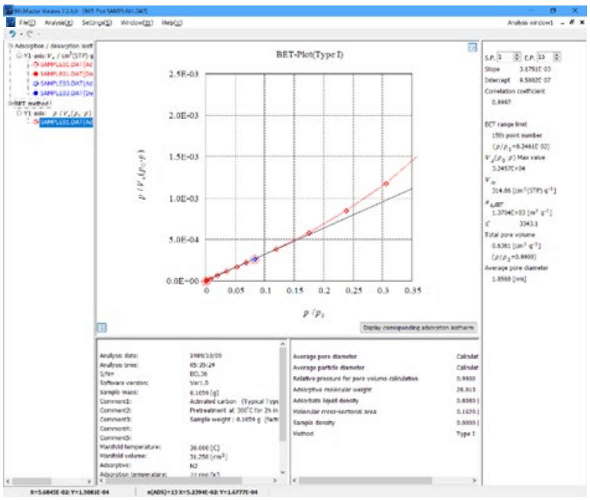
If you select "Release", the relevant graph will be deleted.



Displaying corresponding adsorption isotherm

The adsorption isotherm in the range of using for the currently analyzed graph data is displayed on another window.

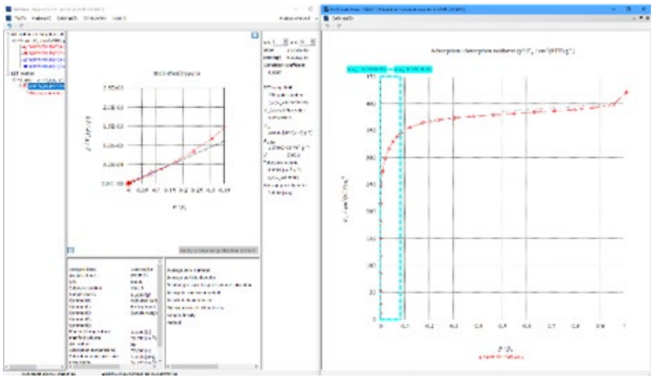
1 Click Display corresponding adsorption isotherm button located on the buttom right of the analyzed graph.



2 The adsorption / desorption isotherm for the analyzed graph data is displayed next to the graph.

The range of using for the analyzed graph is displayed surrounded by a light blue frame.

If a measurement point on the adsorption isotherm or an analysis point on the analyzed graph is selected, the point corresponding to selected point is displayed on another window.



Saving and printing analysis results

Graphs and numerical analysis data can b e 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.

Save analysis data

Save analysis data (numerical data)

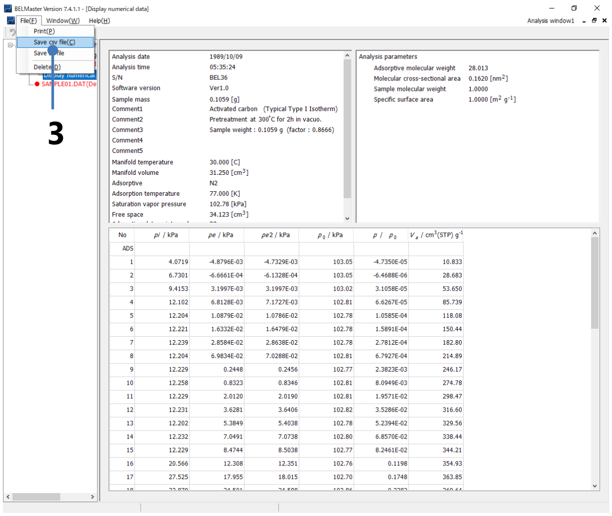
Numerical data from an analysis data can be saved in a file.

1 Display the numerical data you want to save.

→ Display numerical data
P.35 "Display the numerical values of data on the graph"

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

3 Select “File(F)” and “Save csv file(C)” from the data window menu.



Analysis date 1989/10/09
Analysis time 05:35:24
S/N BEL36
Software version Ver1.0
Sample mass 0.1059 [g]
Comment1 Activated carbon (Typical Type I Isotherm)
Comment2 Pretreatment at 300°C for 2h in vacuo.
Comment3 Sample weight : 0.1059 g (factor : 0.8666)
Comment4
Comment5
Manifold temperature 30.000 [C]
Manifold volume 31.250 [cm^3]
Adsorptive N2
Adsorption temperature 77.000 [K]
Saturation vapor pressure 102.78 [kPa]
Free space 34.123 [cm^3]

Analysis parameters
Adsorptive molecular weight 28.013
Molecular cross-sectional area 0.1620 [nm^2]
Sample molecular weight 1.0000
Specific surface area 1.0000 [m^2 g^{-1}]

No	pi / kPa	pe / kPa	$pe2$ / kPa	p_0 / kPa	p / p_0	V_a / cm^3(STP) g^{-1}
ADS						
1	4.0719	-4.8796E-03	-4.7329E-03	103.05	-4.7350E-05	10.833
2	6.7301	-6.6661E-04	-6.1328E-04	103.05	-6.4688E-06	28.683
3	9.4153	3.1997E-03	3.1997E-03	103.02	3.1058E-05	53.650
4	12.102	6.8128E-03	7.1727E-03	102.81	6.6267E-05	85.739
5	12.204	1.0879E-02	1.0786E-02	102.78	1.0585E-04	118.08
6	12.221	1.6332E-02	1.6479E-02	102.78	1.5891E-04	150.44
7	12.239	2.8584E-02	2.8638E-02	102.78	2.7812E-04	182.80
8	12.204	6.9834E-02	7.0288E-02	102.81	6.7927E-04	214.89
9	12.229	0.2448	0.2456	102.77	2.3823E-03	246.17
10	12.258	0.8323	0.8346	102.81	8.0949E-03	274.78
11	12.229	2.0120	2.0190	102.81	1.9571E-02	298.47
12	12.231	3.6281	3.6406	102.82	3.5286E-02	316.60
13	12.202	5.3849	5.4038	102.78	5.2394E-02	329.56
14	12.232	7.0491	7.0738	102.80	6.8570E-02	338.44
15	12.229	8.4744	8.5038	102.77	8.2461E-02	344.21
16	20.566	12.308	12.351	102.76	0.1198	354.93
17	27.525	17.955	18.015	102.70	0.1748	363.85

4 The “Save As” window will be shown.

Specify a folder to save the file in and enter a file name and click the Save button.

The software will save the numerical data form the currently active data window to a file.

5 The numerical data are stored in CSV format, so that they can be used with other softwares.

Conversion of measurement data to AIF file

Measurement data files output from adsorption measurement instruments including BELSORP are in each manufacturer's proprietary file format.

BELMaster can save the measurement data measured by the BELSORP series in a standardized file format (AIF, Adsorption Information Format).

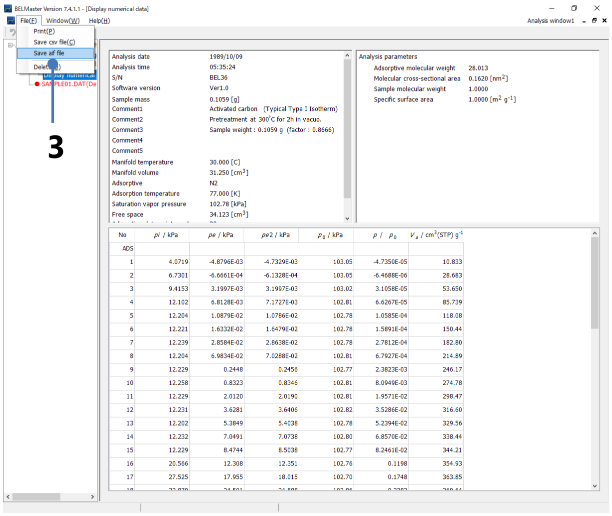
1 Display the numerical data you want to save.

→ Display numerical data

P.35 "Display the numerical values of data on the graph”

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

3 Select “File(F)” and “Save aif file” from the data window menu.



Analysis date	1989/10/09
Analysis time	05:35:24
S/N	BEL36
Software version	Ver1.0
Sample mass	0.1059 [g]
Comment1	Activated carbon (Typical Type I Isotherm)
Comment2	Pretreatment at 300˚C for 2h in vacuo.
Comment3	Sample weight : 0.1059 g (factor : 0.8666)
Comment4	
Comment5	
Manifold temperature	30.000 [C]
Manifold volume	31.250 [cm^3]
Adsorptive	N2
Adsorption temperature	77.000 [K]
Saturation vapor pressure	102.78 [kPa]
Free space	34.123 [cm^3]

Analysis parameters

Adsorptive molecular weight	28.013
Molecular cross-sectional area	0.1620 [nm^2]
Sample molecular weight	1.0000
Specific surface area	1.0000 [m^2 g^{-1}]

No	pi / kPa	pe / kPa	$pe2$ / kPa	p_0 / kPa	p / p_0	V_a / cm^3(STP) g^{-1}
ADS						
1	4.0719	-4.8796E-03	-4.7329E-03	103.05	-4.7350E-05	10.833
2	6.7301	-6.6661E-04	-6.1328E-04	103.05	-6.4688E-06	28.683
3	9.4153	3.1997E-03	3.1997E-03	103.02	3.1058E-05	53.650
4	12.102	6.8128E-03	7.1727E-03	102.81	6.6267E-05	85.739
5	12.204	1.0879E-02	1.0786E-02	102.78	1.0585E-04	118.08
6	12.221	1.6332E-02	1.6479E-02	102.78	1.5891E-04	150.44
7	12.239	2.8584E-02	2.8638E-02	102.78	2.7812E-04	182.80
8	12.204	6.9834E-02	7.0288E-02	102.81	6.7927E-04	214.89
9	12.229	0.2448	0.2456	102.77	2.3823E-03	246.17
10	12.258	0.8323	0.8346	102.81	8.0949E-03	274.78
11	12.229	2.0120	2.0190	102.81	1.9571E-02	298.47
12	12.231	3.6281	3.6406	102.82	3.5286E-02	316.60
13	12.202	5.3849	5.4038	102.78	5.2394E-02	329.56
14	12.232	7.0491	7.0738	102.80	6.8570E-02	338.44
15	12.229	8.4744	8.5038	102.77	8.2461E-02	344.21
16	20.566	12.308	12.351	102.76	0.1198	354.93
17	27.525	17.955	18.015	102.70	0.1748	363.85

4 The “Save As” window will be shown.

Specify a folder to save the file in and enter a file name and click the Save button.

The software will save the measurement data form the currently active data window to an aif file.

For more information on AIF (Adsorption Information Format), refer to the following.

- J. D. Evans et al., *Langmuir*, **37**, 4222 (2021)
- https://adsorptioninformationformat.com/

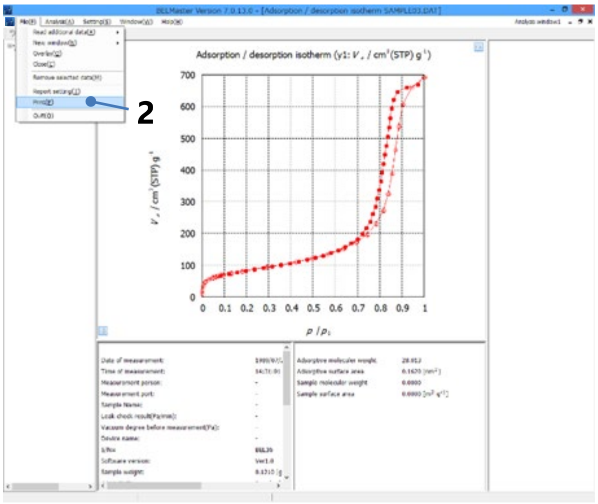
Printing analysis data

Print analysis data (graph)

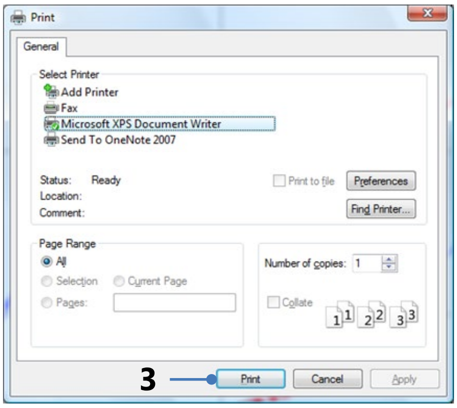
A graph of an analysis data can be printed on paper.

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

2 Select “File(F)” and “Print(P)” from the analysis window menu.

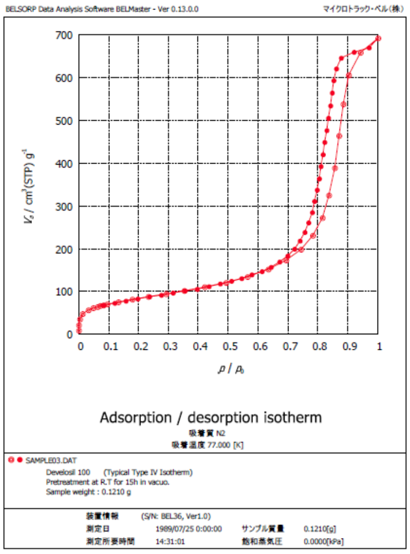


3 The “Print” window shown on the right will appear. Specify a printer type and print direction. Then click the Print button. The software will print the specified graph.



Status: Ready
Location:
Comment:
● All
Number of copies: 1

4 The data analysis (figure) are printed using the format shown on the right.



Adsorption / desorption isotherm
吸着質 N2
吸着温度 77.000 [K]

SAMPLE03.DAT
Develosil 100 (Typical Type IV Isotherm)
Pretreatment at R.T for 15h in vacuo.
Sample weight : 0.1210 g

装置情報	(S/N: BEL36, Ver1.0)		
測定日	1989/07/25 0:00:00	サンプル質量	0.1210[g]
測定所要時間	14:31:01	飽和蒸気圧	0.0000[kPa]

Print analysis data (numerical data)

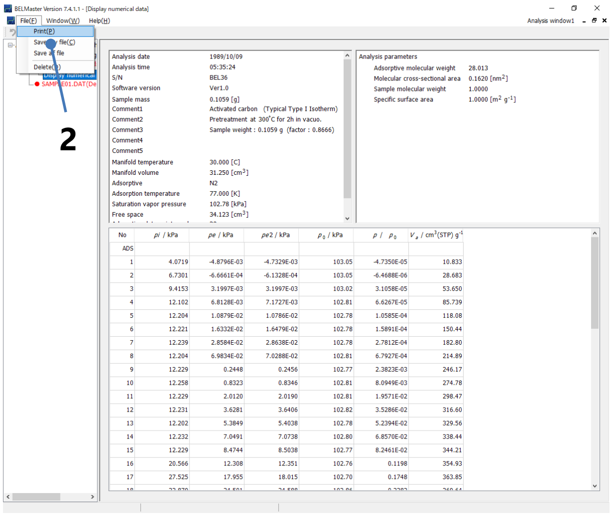
Numerical data from an analysis data can b e printed.

1 Activates the data window you want to print.

→ Display numerical data

P.35 “Display the numerical values of data on the graph”

2 Select “File(F)” and “Print(P)” from the data window menu.



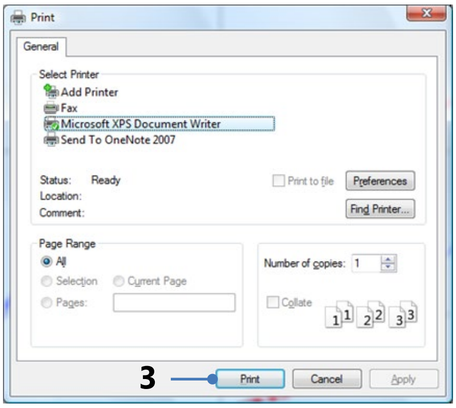
Analysis date	1989/10/09
Analysis time	05:35:24
S/N	BEL36
Software version	Ver1.0
Sample mass	0.1059 [g]
Comment1	Activated carbon (Typical Type I Isotherm)
Comment2	Pretreatment at 300˚C for 2h in vacuo.
Comment3	Sample weight : 0.1059 g (factor : 0.8666)
Comment4	
Comment5	
Manifold temperature	30.000 [C]
Manifold volume	31.250 [cm^3]
Adsorptive	N2
Adsorption temperature	77.000 [K]
Saturation vapor pressure	102.78 [kPa]
Free space	34.123 [cm^3]

Analysis parameters

Adsorptive molecular weight	28.013
Molecular cross-sectional area	0.1620 [nm^2]
Sample molecular weight	1.0000
Specific surface area	1.0000 [m^2 g^{-1}]

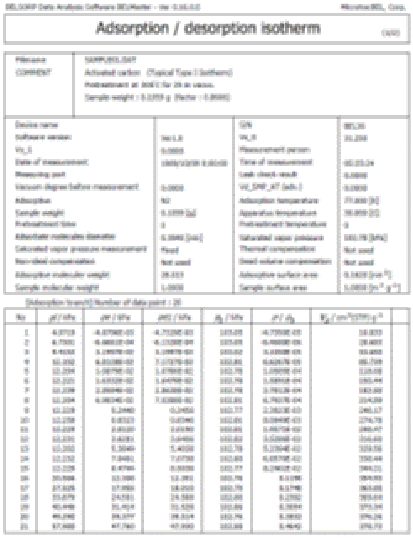
No	pi / kPa	pe / kPa	$pe2$ / kPa	p_0 / kPa	p / p_0	V_a / cm^3(STP) g^{-1}
ADS						
1	4.0719	-4.8796E-03	-4.7329E-03	103.05	-4.7350E-05	10.833
2	6.7301	-6.6661E-04	-6.1328E-04	103.05	-6.4688E-06	28.683
3	9.4153	3.1997E-03	3.1997E-03	103.02	3.1058E-05	53.650
4	12.102	6.8128E-03	7.1727E-03	102.81	6.6267E-05	85.739
5	12.204	1.0879E-02	1.0786E-02	102.78	1.0585E-04	118.08
6	12.221	1.6332E-02	1.6479E-02	102.78	1.5891E-04	150.44
7	12.239	2.8584E-02	2.8638E-02	102.78	2.7812E-04	182.80
8	12.204	6.9834E-02	7.0288E-02	102.81	6.7927E-04	214.89
9	12.229	0.2448	0.2456	102.77	2.3823E-03	246.17
10	12.258	0.8323	0.8346	102.81	8.0949E-03	274.78
11	12.229	2.0120	2.0190	102.81	1.9571E-02	298.47
12	12.231	3.6281	3.6406	102.82	3.5286E-02	316.60
13	12.202	5.3849	5.4038	102.78	5.2394E-02	329.56
14	12.232	7.0491	7.0738	102.80	6.8570E-02	338.44
15	12.229	8.4744	8.5038	102.77	8.2461E-02	344.21
16	20.566	12.308	12.351	102.76	0.1198	354.93
17	27.525	17.955	18.015	102.70	0.1748	363.85

3 The “Print” window shown on the right will appear. Specify a printer type and print direction. Then click the Print button. The software will print the specified numerical data.



Status: Ready
Location:
Comment:
● All
Number of copies: 1

4 Numerical data are printed using the format shown on the right.

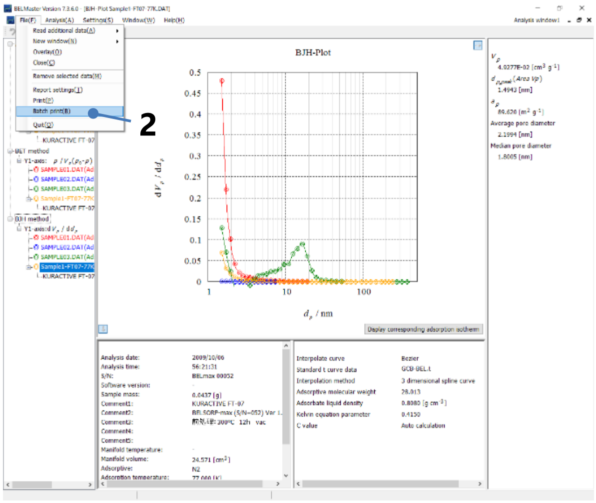


Batch printing analysis data

Multiple graphs or numeric data of an anal ysis data can be printed on paper.

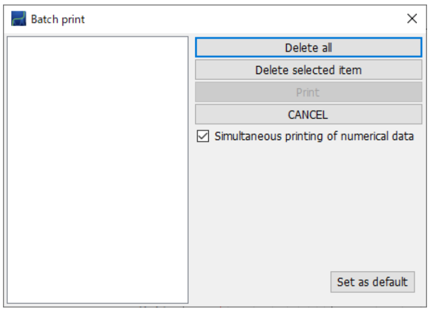
1 Select the analysis window containing the graph or the numerical data you want to print.

2 Select “File(F)” and “Batch print(P)” from the analysis window menu.

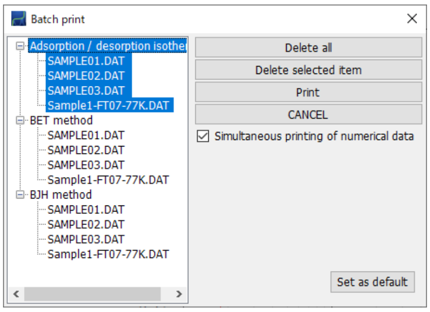


3 The “Batch print” window shown on the right will appear. Drag and drop the data you want to print from the analysis window to the "Batch print" window and copy the data.

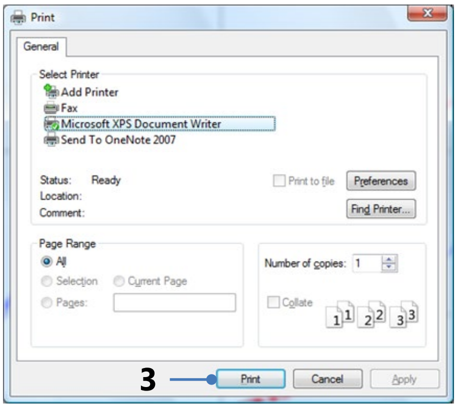
- The data at the time of copying will be printed. After the data is copied, any setting change will not be reflected in printing.



4 Click the Print button. The “Print” window shown.

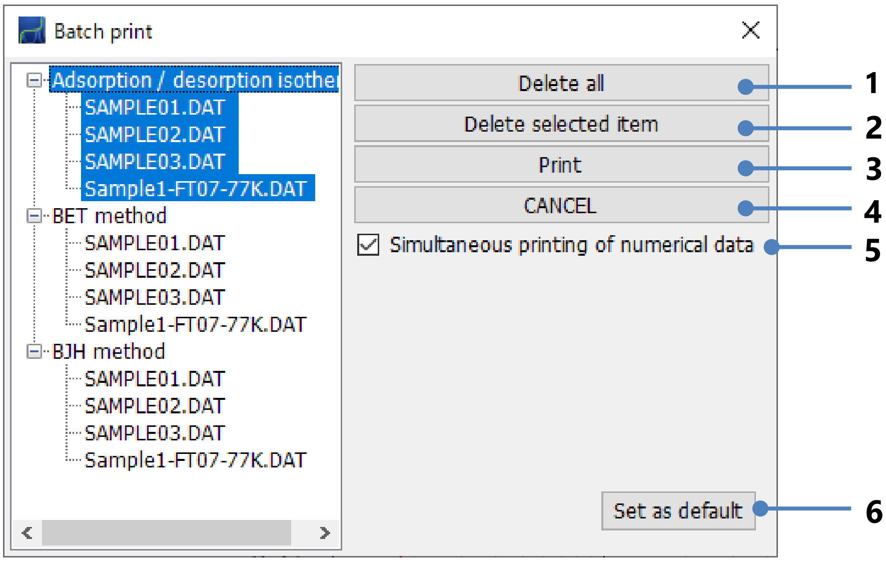


5 Specify a printer type and print direction. Then click the Print button. The software will print the specified graphs or the numerical data.



6 The analysis data (graphs or numerical data) are printed in the same format as normal printing function.

Other functions of the “Batch print” window are as follows.



1	Clear copied data.
2	Clear only selected items.
3	Print the displayed data ina a batch.
4	Close the “Batch print” window.
5	Simultaneously print numerical data for all analysis data.
6	Save the setting of whether to print numerical data at the same time as the default.

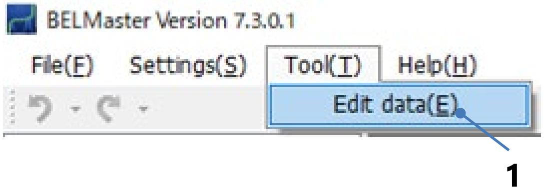
Edit data

The data items that were set when taking measurements can be edited and saved.

“Edit data” is only possible when the main window is displayed. If an analysis window or a data window is open, you cannot edit the data. Close any opened analysis windows and data window and try editing the data again.

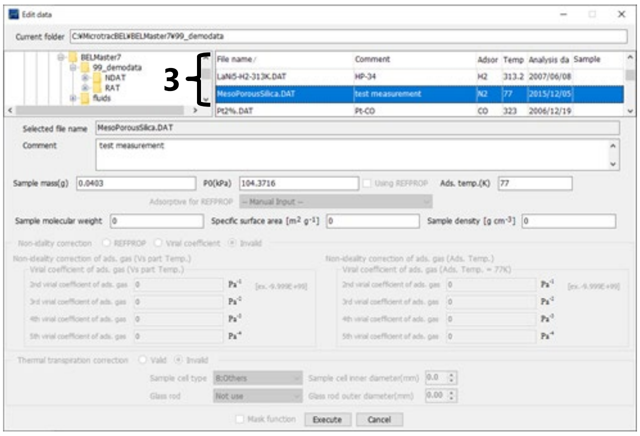
- Edit data” can be used for .DAT or .NDAT file.
  Data for adsorption rate analysis (.RAT and .NRAT file) can not be edited.

1 Select “Tool(T)” and “Edit data(E)” from the main window menu.



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

3 Select the file you want to edit from the list of data files.



Current folder: C:¥MicrotracBEL¥BELMaster7¥99_demodata

File name	Comment	Adsor	Temp	Analysis da	Sample
LaNi5-H2-313K.DAT	HP-34	H2	313.2	2007/06/08	
MesoPorousSilica.DAT	test measurement	N2	77	2015/12/05	
Pt2%.DAT	Pt-CO	CO	323	2006/12/19	

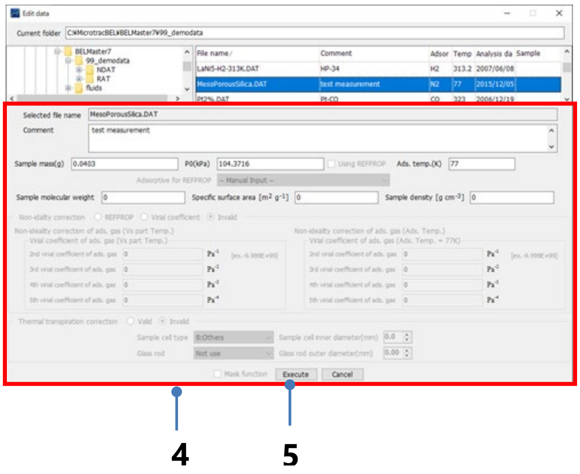
Selected file name: MesoPorousSilica.DAT
Comment: test measurement
Sample mass(g): 0.0403
P0(kPa): 104.3716
Ads. temp.(K): 77
Sample molecular weight: 0
Specific surface area [$m^2\ g^{-1}$]: 0
Sample density [$g\ cm^{-3}$]: 0
2nd virial coefficient of ads. gas: 0 Pa^{-1}
3rd virial coefficient of ads. gas: 0 Pa^{-2}
4th virial coefficient of ads. gas: 0 Pa^{-3}
5th virial coefficient of ads. gas: 0 Pa^{-4}
2nd virial coefficient of ads. gas: 0 Pa^{-1}
3rd virial coefficient of ads. gas: 0 Pa^{-2}
4th virial coefficient of ads. gas: 0 Pa^{-3}
5th virial coefficient of ads. gas: 0 Pa^{-4}
Sample cell type: 8:Others
Sample cell inner diameter(mm): 0.0
Glass rod: Not use
Glass rod outer diameter(mm): 0.00

Edit DAT file

4 The data items specified when measurements ware taken will be displayed. Edit any item you want to change. The items which are able to be edited in DAT file are below.

The items which are not able to be edited are by grayed out.

- Comment [Measurement result is not affected.]
- Sample mass [Amount adsorbed is affetcted.]
- P0 (Saturation vapor pressure)
  [Relative pressure is affetcted.]
- Ads. temp. [Measurement result is not affected.
  Analysis results such as isosteric
  heat of adsorption may be affetcted.]



Current folder C:¥MicrotracBEL¥BELMaster7¥99_demodata

File name	Comment	Adsor	Temp	Analysis da	Sample
LaNi5-H2-313K.DAT	HP-34	H2	313.2	2007/06/08	
MesoPorousSilica.DAT	test measurement	N2	77	2015/12/05	
Pt2%.DAT	Pt-CO	CO	323	2006/12/19	

Selected file name MesoPorousSilica.DAT

Comment test measurement

Sample mass(g) 0.0403 P0(kPa) 104.3716 ☐ Using REFPROP Ads. temp.(K) 77

Adsorptive for REFPROP -- Manual Input --

Sample molecular weight 0 Specific surface area [$m^2\ g^{-1}$] 0 Sample density [$g\ cm^{-3}$] 0

Non-ideality correction ○ REFPROP ○ Virial coefficient ● Invalid

Non-ideality correction of ads. gas (Vs part Temp.)

Virial coefficient of ads. gas (Vs part Temp.)

2nd virial coefficient of ads. gas 0 Pa^{-1} [ex. -9.999E+99]

3rd virial coefficient of ads. gas 0 Pa^{-2}

4th virial coefficient of ads. gas 0 Pa^{-3}

5th virial coefficient of ads. gas 0 Pa^{-4}

Non-ideality correction of ads. gas (Ads. Temp.)

Virial coefficient of ads. gas (Ads. Temp. = 77K)

2nd virial coefficient of ads. gas 0 Pa^{-1} [ex. -9.999E+99]

3rd virial coefficient of ads. gas 0 Pa^{-2}

4th virial coefficient of ads. gas 0 Pa^{-3}

5th virial coefficient of ads. gas 0 Pa^{-4}

Thermal transpiration correction ○ Valid ● Invalid

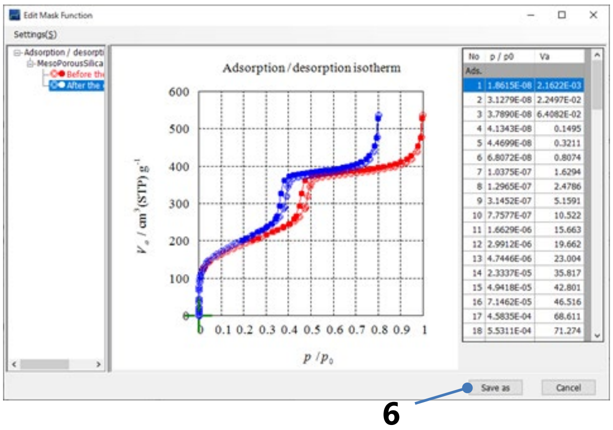
Sample cell type 8:Others Sample cell inner diameter(mm) 0.0

Glass rod Not use Glass rod outer diameter(mm) 0.00

5 To edit measurement data by the conditions entered, click the Execute button. To close the window, select the Cancel button.

6 Adsorption and desorption isotherm lines after and before editing are displayed. (Before change: Red, After change: Blue)

Click the Save as button, if there is no problem. The data can be saved with a specified file name.



No	p / p0	Va
Ads.		
1	1.8615E-08	2.1622E-03
2	3.1279E-08	2.2497E-02
3	3.7890E-08	6.4082E-02
4	4.1343E-08	0.1495
5	4.4699E-08	0.3211
6	6.8072E-08	0.8074
7	1.0375E-07	1.6294
8	1.2965E-07	2.4786
9	3.1452E-07	5.1591
10	7.7577E-07	10.522
11	1.6629E-06	15.663
12	2.9912E-06	19.662
13	4.7446E-06	23.004
14	2.3337E-05	35.817
15	4.9418E-05	42.801
16	7.1462E-05	46.516
17	4.5835E-04	68.611
18	5.5311E-04	71.274

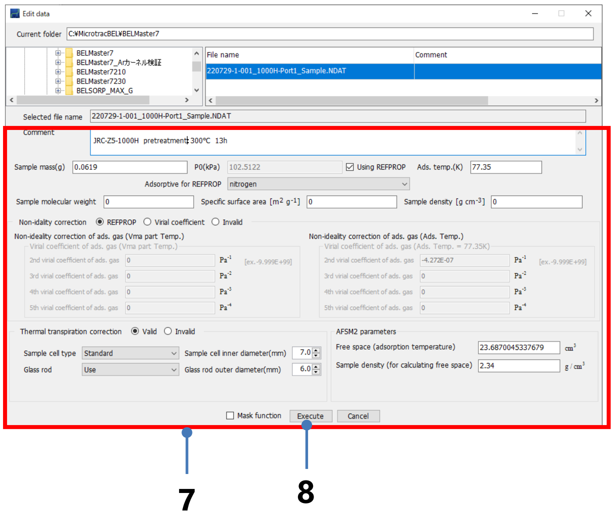
Edit NDAT file

7 The data items specified when measurements ware taken will be displayed.

Edit any item you want to change.

All the items are able to be edited in NDAT file.

The details of each data is shown as follows.



Current folder: C:¥MicrotracBEL¥BELMaster7
220729-1-001_1000H-Port1_Sample.NDAT
Selected file name: 220729-1-001_1000H-Port1_Sample.NDAT
Comment: JRC-Z5-1000H pretreatment 300℃ 13h
Sample mass(g): 0.0619
P0(kPa): 102.5122
☑ Using REFPROP
Ads. temp.(K): 77.35
Adsorptive for REFPROP: nitrogen
Sample molecular weight: 0
Specific surface area [m^2 g^{-1}]: 0
Sample density [g cm^{-3}]: 0
Non-idality correction: ● REFPROP ○ Virial coefficient ○ Invalid
Non-ideality correction of ads. gas (Vma part Temp.)
Virial coefficient of ads. gas (Vma part Temp.)
2nd virial coefficient of ads. gas: 0 Pa^{-1} [ex.-9.999E+99]
3rd virial coefficient of ads. gas: 0 Pa^{-2}
4th virial coefficient of ads. gas: 0 Pa^{-3}
5th virial coefficient of ads. gas: 0 Pa^{-4}
Non-ideality correction of ads. gas (Ads. Temp.)
Virial coefficient of ads. gas (Ads. Temp. = 77.35K)
2nd virial coefficient of ads. gas: -4.272E-07 Pa^{-1} [ex.-9.999E+99]
3rd virial coefficient of ads. gas: 0 Pa^{-2}
4th virial coefficient of ads. gas: 0 Pa^{-3}
5th virial coefficient of ads. gas: 0 Pa^{-4}
Thermal transpiration correction: ● Valid ○ Invalid
Sample cell type: Standard
Sample cell inner diameter(mm): 7.0
Glass rod: Use
Glass rod outer diameter(mm): 6.0
AFSM2 parameters
Free space (adsorption temperature): 23.6870045337679 cm^3
Sample density (for calculating free space): 2.34 g / cm^3

Item	Summary
Comment	Edit comment in data file. Measurement result is not affected.
Sample mass [g]	Edit sample mass. Amount adsorbed is affetced.
P0 [kPa]	Edit saturation vapor pressure. Relative pressure is affetcted. Even in the data which is measured with saturation vapor pressure, if this item is altered, the data is recalculated by using fixed value. (If you need to use the saturation vapor value during the measurement, don't edit this item.)
Using REFPROP	Saturation vapor pressure is calculated from selected adsorptive and adsorption temperature automatically. In the case that [--Manual Input--] is selected as adsorptive, this function is not able to be used. Also, in the case that adsorption tempereateure is below triple point of adsorptive, this is not able to be used.
Adosorptive for REFPROP	Select adsorptive from the list in the case that you use the function for calculation of saturation vapor pressure or non-ideality correction by REFPROP. Confirm that selected adsorptive corresponds to adsorptive in measured data. In the case of [--Manual Input--], this function is not able to be used.
Ads. temp. [K]	Edit adsorption temperature. Amount adsorbed is affected unlike the case of DAT file.
Sample molecular weight	Edit sample molecular weicht. Although amount adsorbed is not affetced, analysis result like PCT curve is affected.

Item	Summary		
Specific surface area $[m^2\ g^{-1}]$	Edit specific surface area of sample. Although amount adsorbed is not affected, analysis result in the case that [molec nm^{-2}] in Y-axis setting in “adsorption / desorption” is selected is affected.		
Sample density $[g\ cm^{-3}]$	Edit density of sample. Although amount adsorbed is not affected, analysis result of average particle diameter calculated from “BET plot” is affected.		
Non-ideality correction of ads. gas	Select whether to calculate including non-ideality correction.		
		REFPROP	Select this button in the case that you use the function for calculation of compression factor for non-ideality correction by REFPROP. The software calculates compression factor from manifold tempertrure or adsorption temperature and pressure of each measurement point, and correct data. This button is not able to be selected in the case that [--Manual Input--] in “Adsorptive for REFPROP” is selected. For just data mesured with saturation vapor pressure, adsorption temperature for each point is calculated automatically, and compression factor is obtained from calculated adsorption temperature.
		Virial coefficient	Select this button in the case that you use the virial coefficients for calculation of compression factor for non-ideality correction. The software calculates compression factor from pressure of each measurement point and virial coefficients, and correct data. In the case that you select “Virial coefficient”, input the second to the fifth virial coefficients for each temperature.
		Invalid	Select this button in the case that you don’t calculate the compression factor.
Thermal transpiration correction	Select whether to calculate including thermal transpiration correction. In the case of “Invalid”, following items are not be altered. In the case of “Valid”, set following items.		
		Sample cell type	Input inner diameter of sample cell.
		Glass rod	Input outer diameter of glass rod.
AFSM2 parameters	The free space of the sample cell and sample density can be changed and recalculated in the data measured with AFSM2.		
		Free space (Adsortption temperature)	Enter the free space of the blank sample cell at the adsorption temperature.
		Sample density (for calculating free space)	Enter the sample density.

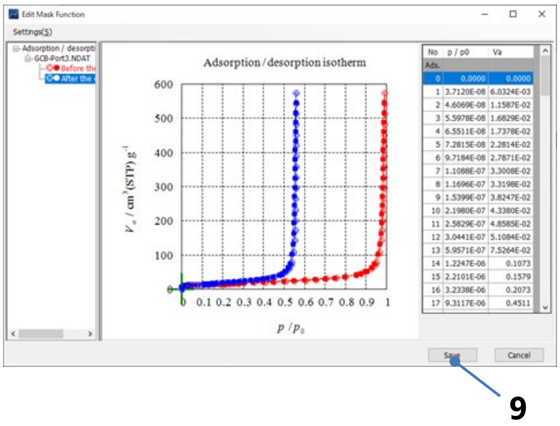
Item	Summary
Mask function	Select thiis check box in the case that you would like not to display any data after editing data. You could select the data point for non-display in the following window.

8 To edit measurement data by the conditions entered, click the Execute button. To close the window, select the Cancel button.

9 Adsorption and desorption isotherm lines after and before editing are displayed. (Before change: Red, After change: Blue)

In the case that the “Mask function” is valid, remove the check from checkboxes for data points which you would like not to display.

Click the Save button, if there is no problem. The data can be saved with a specified file name.



No	p / p0	Va
Ads.		
0	0.0000	0.0000
1	3.7120E-08	6.0324E-03
2	4.6069E-08	1.1587E-02
3	5.5978E-08	1.6829E-02
4	6.5511E-08	1.7378E-02
5	7.2815E-08	2.2814E-02
6	9.7184E-08	2.7871E-02
7	1.1088E-07	3.3008E-02
8	1.1696E-07	3.3198E-02
9	1.5399E-07	3.8247E-02
10	2.1980E-07	4.3380E-02
11	2.5829E-07	4.8585E-02
12	3.0441E-07	5.1084E-02
13	5.9571E-07	7.5264E-02
14	1.2247E-06	0.1073
15	2.2101E-06	0.1579
16	3.2338E-06	0.2073
17	9.3117E-06	0.4511

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. “P.69 “Adsorption/desorption isotherm”” and later describe the operation methods while showing descriptions and sample examples for each analysis method.

Adsorption isotherm

In physical adsorption, adsorption isotherms can be classified, as shown in the table below. Table 1 shows the types and features, as well an adsorbent example.

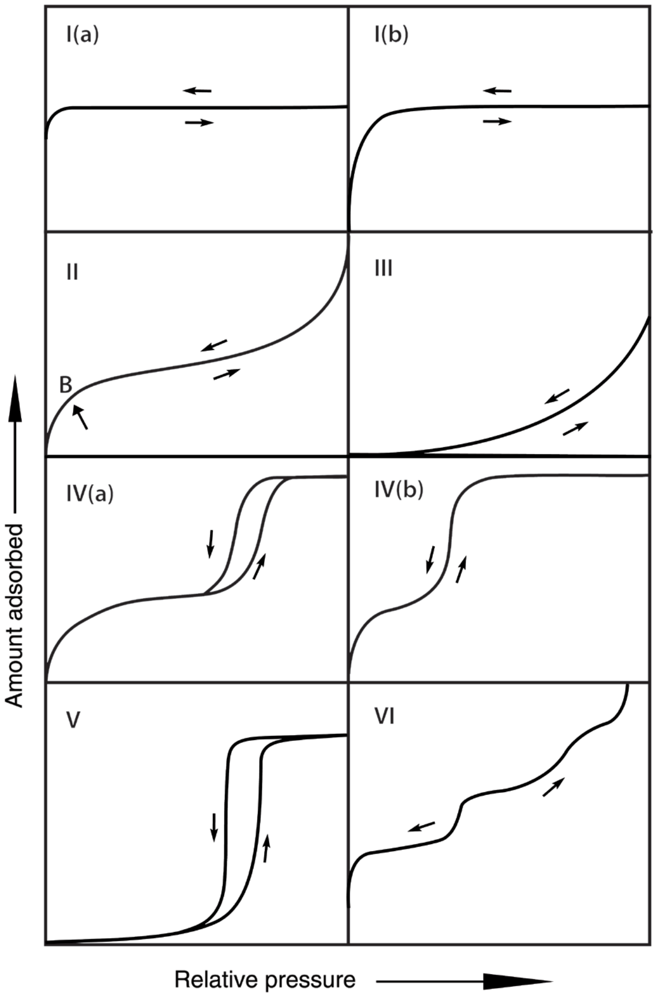


Figure 1: IUPAC classification of adsorption

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

Table 2: IUPAC classification of pores

Pore name	Pore diameter / nm
Micropore	Up to 2
Mesopore	2 to 50
Macropore	50 or up

Adsorption isotherms are classified as shown in table 1 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”, 2nd Ed., F. Rouquerol, J Rouquerol & K. S. W. Sing, Academic Press INC., London (2012)

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

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	$2t$ [nm]	Pore shape: Slit Pore diameter.: 0.7 to 2.0 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 width: 2.0 nm or less
	Micropore distribution peak	HK plot	W_{peak} [nm]	
	Micropore distribution curve	SF plot	Micropore range	Pore shape: Cylinder Pore diameter: 2.0 nm or less
	Micropore distribution peak	SF plot	$d_{p,\,peak}$ or $r_{p,\,peak}$ [nm]	
	Micropore distribution curve	CY plot	Micropore range	Pore shape: Cage Pore diameter: 2.0 nm or less
	Micropore distribution peak	CY 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、INNES 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 “Adsorption/desorption isotherm” or later. Depending on the setting, “nm” may be changed to “Å”.

Table 4: Using symbols in the BELMaster manual

Method	Symbol	Unit	Mean
Adsorption / desorption isotherm	$p\,/\,p_0$	–	Relative pressure (p_0 is saturation vapor pressure of the adsorptive at measurement temperature.)
	p	kPa, Torr	Absolute pressure
	RH	%	Relative humidity
	V_{a}	$\mathrm{cm^3(STP)\ g^{-1}}$	Amount adsorbed expressed in the gas volume at the standard state (STP: 273.15 K, 101.3 kPa) on 1 g of adsorbent
	m_{a}	$\mathrm{mg\ g^{-1}}$	Mass adsorbed on 1 g of adsorbent
	Γ	$\mathrm{molec\ nm^{-2}}$	Numbers of molecules adsorbed on a unit surface area of adsorbent
	n_{a}	$\mathrm{mol\ mol^{-1}}$	Amount adsorbed on 1 mol of adsorbent expressed in mol
	n_{a}	$\mathrm{mol\ g^{-1}}$	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 V_{a} ($p\,/\,p_0$ = 0.4).
Adsorption rate analysis	$K_{\mathrm{s}}\,a_{\mathrm{p}}$	$\mathrm{sec^{-1}}$	Mass transfer coefficient
	$D_{\mathrm{s}}\,/\,R^2$	$\mathrm{sec^{-1}}$	Surface diffusion coefficient
	α		Separation factor (= $V\,/\,W\cdot H$)
PCT curve	$H\,/\,M$	–	Amount (mol) of hydrogen occluded by 1 mol of sample (metal).
	wt	%	Amount (%) of hydrogen occluded by 1 g of sample (metal).
	V_{a}	$\mathrm{cm^3(STP)\ g^{-1}}$	Specific amount adsorbed expressed in the gas volume at the standard state (STP: 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 vapor pressure of the adsorptive at measurement temperature.)
	V_{m}	$\mathrm{cm^3\ (STP)\ g^{-1}}$	Monolayer amount
	$\alpha_{\mathrm{s\ BET}}$	$\mathrm{m^2\ g^{-1}}$	BET specific surface area
	C	–	BET parameter
	σ	$\mathrm{nm^2}$	Molecular cross-sectional area
	M_{g}	–	Molecular weight of adsorptive
	L	–	Avogadro constant
	ρ_{a}	$\mathrm{g\ cm^{-3}}$	Adsorbate liquid density
	ρ_{s}	$\mathrm{g\ cm^{-3}}$	Density of sample

Method	Symbol	Unit	Mean
BET analysis	V_{p}	$\mathrm{cm^3\ g^{-1}}$	Total pore volume
	d_{p}	nm	Mean pore diameter
	l	nm	Mean particle size
Langmuir plot	p	kPa, Torr	Absolute pressure
	V_{m}	$\mathrm{cm^3(STP)\ g^{-1}}$	Monolayer amount
	$\alpha_{\mathrm{s\ Lang}}$	$\mathrm{m^2\ g^{-1}}$	Langmuir specific surface area
	B	–	Ratio of rate constant (adsorption / desorption)
	σ	$\mathrm{nm^2}$	Molecular cross-sectional area
Freundlich plot	p	kPa, Torr	Absolute pressure
	V_{m}	$\mathrm{cm^3(STP)\ g^{-1}}$	Monolayer amount
	$a_{\mathrm{s,Freundlich}}$	$\mathrm{m^2\ g^{-1}}$	Freundlich specific surface area
	q_{m}	$\mathrm{kJ\ mol^{-1}}$	Adsorption heat at coverage $\theta = 0.3679$
	σ	$\mathrm{nm^2}$	Molecular cross-sectional area
BJH/CI/DH plot	r_{p}	nm	Pore radius (cylindrical shape)
	d_{p}	nm	Pore diameter (cylindrical shape)
	$\mathrm{d}V_{\mathrm{p}} / \mathrm{d}r_{\mathrm{p}}$	$\mathrm{cm^3\ g^{-1}\ nm^{-1}}$	Pore area distribution
	$\mathrm{d}V_{\mathrm{p}} / \mathrm{dlog}r_{\mathrm{p}}$	$\mathrm{cm^3\ g^{-1}}$	Pore volume distribution
	$\mathrm{d}V_{\mathrm{p}} / \mathrm{d}d_{\mathrm{p}}$	$\mathrm{cm^3\ g^{-1}\ nm^{-1}}$	Pore area distribution
	$\mathrm{d}V_{\mathrm{p}} / \mathrm{dlog}d_{\mathrm{p}}$	$\mathrm{cm^3\ g^{-1}}$	Pore volume distribution
	ΣV_{p}	$\mathrm{cm^3\ g^{-1}}$	Cumulative pore volume
	$\mathrm{d}a_{\mathrm{p}} / \mathrm{d}r_{\mathrm{p}}$	$\mathrm{m^2\ g^{-1}\ nm^{-1}}$	Pore length distribution
	$\mathrm{d}a_{\mathrm{p}} / \mathrm{dlog}r_{\mathrm{p}}$	$\mathrm{m^2\ g^{-1}}$	Pore area distribution
	$\mathrm{d}a_{\mathrm{p}} / \mathrm{d}d_{\mathrm{p}}$	$\mathrm{m^2\ g^{-1}\ nm^{-1}}$	Pore length distribution
	$\mathrm{d}a_{\mathrm{p}} / \mathrm{dlog}d_{\mathrm{p}}$	$\mathrm{m^2\ g^{-1}}$	Pore area distribution
	Σa_{p}	$\mathrm{cm^3\ g^{-1}}$	Cumulative pore area
	V_{p}	$\mathrm{cm^3\ g^{-1}}$	Pore volume
	a_{p}	$\mathrm{m^2\ g^{-1}}$	Pore specific surface area
INNES plot	dx	nm	Pore width (slit shape)
	$\mathrm{d}V_{\mathrm{p}} / \mathrm{d}dx$	$\mathrm{cm^3\ g^{-1}\ nm^{-1}}$	Pore area distribution
	$\mathrm{d}V_{\mathrm{p}} / \mathrm{dlog}dx$	$\mathrm{cm^3\ g^{-1}}$	Pore volume distribution
	ΣV_{p}	$\mathrm{cm^3\ g^{-1}}$	Cumulative pore volume
	$\mathrm{d}a_{\mathrm{p}} / \mathrm{d}dx$	$\mathrm{m^2\ g^{-1}\ nm^{-1}}$	Pore length distribution
	$\mathrm{d}a_{\mathrm{p}} / \mathrm{dlog}dx$	$\mathrm{m^2\ g^{-1}}$	Pore area distribution
	Σa_{p}	$\mathrm{cm^3\ g^{-1}}$	Cumulative pore area

Method	Symbol	Unit	Mean
INNES plot	V_p	$cm^3\ g^{-1}$	Pore volume
	a_p	$m^2\ g^{-1}$	Pore specific surface area
MP plot	r_p	nm	Pore radius (cylindrical shape)
	d_p	nm	Pore diameter (cylindrical shape)
	$\mathrm{d}V_p / \mathrm{d}r_p$	$cm^3\ g^{-1}\ nm^{-1}$	Pore area distribution
	$\mathrm{d}V_p / \mathrm{dlog}r_p$	$cm^3\ g^{-1}$	Pore volume distribution
	$\mathrm{d}V_p / \mathrm{d}d_p$	$cm^3\ g^{-1}\ nm^{-1}$	Pore area distribution
	$\mathrm{d}V_p / \mathrm{dlog}d_p$	$cm^3\ g^{-1}$	Pore volume distribution
	ΣV_p	$cm^3\ g^{-1}$	Cumulative pore volume
	$\mathrm{d}a_p / \mathrm{d}r_p$	$m^2\ g^{-1}\ nm^{-1}$	Pore length distribution
	$\mathrm{d}a_p / \mathrm{dlog}r_p$	$m^2\ g^{-1}$	Pore area distribution
	$\mathrm{d}a_p / \mathrm{d}d_p$	$m^2\ g^{-1}\ nm^{-1}$	Pore length distribution
	$\mathrm{d}a_p / \mathrm{dlog}d_p$	$m^2\ g^{-1}$	Pore area distribution
	Σa_p	$cm^3\ g^{-1}$	Cumulative pore area
	a_1	$m^2\ g^{-1}$	Total specific surface area
	a_2	$m^2\ g^{-1}$	External specific surface area
	V_p	$cm^3\ g^{-1}$	Pore volume
HK plot	W	nm	Pore width (slit shape)
	$\mathrm{d}V_p / \mathrm{d}W$	$cm^3\ g^{-1}\ nm^{-1}$	Pore area distribution
	$\mathrm{d}V_p / \mathrm{dlog}W$	$cm^3\ g^{-1}$	Pore volume distribution
	ΣV_p	$cm^3\ g^{-1}$	Cumulative pore volume
	$\mathrm{d}a_p / \mathrm{d}W$	$m^2\ g^{-1}\ nm^{-1}$	Pore length distribution
	$\mathrm{d}a_p / \mathrm{dlog}W$	$m^2\ g^{-1}$	Pore area distribution
	Σa_p	$cm^3\ g^{-1}$	Cumulative pore area
	d_a	nm	Adsorptive molecular diameter
	d_s	nm	Adsorbent atom diameter
	N_a	m^{-2}	Number of adsorbate 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
SF plot	r_p	nm	Pore radius (cylindrical shape)
	d_p	nm	Pore diameter (cylindrical shape)

Method	Symbol	Unit	Mean
SF plot	dV_p/dr_p	$cm^3\ g^{-1}\ nm^{-1}$	Pore area distribution
	$dV_p/d\log r_p$	$cm^3\ g^{-1}$	Pore volume distribution
	dV_p/dd_p	$cm^3\ g^{-1}\ nm^{-1}$	Pore area distribution
	$dV_p/d\log d_p$	$cm^3\ g^{-1}$	Pore volume distribution
	ΣV_p	$cm^3\ g^{-1}$	Cumulative pore volume
	da_p/dr_p	$m^2\ g^{-1}\ nm^{-1}$	Pore length distribution
	$da_p/d\log r_p$	$m^2\ g^{-1}$	Pore area distribution
	da_p/dd_p	$m^2\ g^{-1}\ nm^{-1}$	Pore length distribution
	$da_p/d\log d_p$	$m^2\ g^{-1}$	Pore area distribution
	Σa_p	$cm^3\ g^{-1}$	Cumulative pore area
	d_a	nm	Adsorptive molecular diameter
	d_s	nm	Adsorbent atom diameter
	N_a	m^{-2}	Number of adsorbate 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
CY plot	r_p	nm	Pore radius (cage shape)
	d_p	nm	Pore diameter (cage shape)
	dV_p/dr_p	$cm^3\ g^{-1}\ nm^{-1}$	Pore area distribution
	$dV_p/d\log r_p$	$cm^3\ g^{-1}$	Pore volume distribution
	dV_p/dd_p	$cm^3\ g^{-1}\ nm^{-1}$	Pore area distribution
	$dV_p/d\log d_p$	$cm^3\ g^{-1}$	Pore volume distribution
	ΣV_p	$cm^3\ g^{-1}$	Cumulative pore volume
	da_p/dr_p	$m^2\ g^{-1}\ nm^{-1}$	Pore length distribution
	$dA_p/d\log r_p$	$m^2\ g^{-1}$	Pore area distribution
	da_p/dd_p	$m^2\ g^{-1}\ nm^{-1}$	Pore length distribution
	$da_p/d\log d_p$	$m^2\ g^{-1}$	Pore area distribution
	Σa_p	$cm^3\ g^{-1}$	Cumulative pore area
	d_a	nm	Adsorptive molecular diameter
	d_s	nm	Adsorbent atom diamete
	N_a	m^{-2}	Number of adsorbate molecules adsorbed per unit surface area
	N_s	m^{-2}	Number of adsorbent atoms per unit surface area

Method	Symbol	Unit	Mean
CY plot	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
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	$cm^3\ (STP)\ g^{-1}$	Amount adsorbed expressed in the gas volume at the standard state (STP: 273.15 K, 101.3 kPa) on 1 g of sample
α_s plot	α_s	–	A value obtained by dividing an adsorption amount at arbitrary equilibrium pressure by adsorption amount V_a (p/p_0 = 0.4).
	V_a	$cm^3(STP)\ g^{-1}$	Amount adsorbed expressed in the gas volume at the standard state (STP: 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
DA plot	V_p	$cm^3\ g^{-1}$	Pore volume
	E_0	$kJ\ mol^{-1}$	Adsorption potential energy
Metal dispersion analysis	N_g	$mol\ g^{-1}$	Number of moles of the adsorbate on supported metal catalyst 1g
	N_s	$mol\ g^{-1}$	Number of moles 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	%	Supported metal content
	k_{sf}	–	Stoichiometry factor
	D_m	%	Metal dispersion
	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 sample 1 g
	a_s (Metal)	$m^2\ g^{-1}$	Supported metal surface area per supported metal 1 g
	l_m	nm	Average metal particle size
Isosteric heat of adsorption	Q_{st}	$kJ\ mol^{-1}$	Isosteric heat of adsorption

Method	Symbol	Unit	Mean
Isosteric heat of adsorption	V_a	cm^3 (STP) g^{-1}	Specific amount adsorbed expressed in the gas volume at the standard state (STP: 273.15 K, 101.3 kPa) on 1 g of adsorbent.
	p	kPa,Torr	Absolute pressure
Fractal dimension	p / p_0	–	Relative pressure (p_0 is saturation vapor pressure of adsorbate at measuring temperature)
	D		Fractal dimension
Molecular probe method	W_0	$cm^3\ g^{-1}$	Pore volume
	D_S	nm	Short axis length of smallest projection cross sectional area (adsorptive)
	D_L	nm	Long axis length of smallest projection cross sectional area (adsorptive)
	d_m	nm	Adsorptive molecular diameter
	d_p	nm	Pore diameter (cylindrical or cage shape)
	r_p	nm	Pore radius (cylindrical or cage shape)
	W	nm	Pore width (slit shape)
NLDFT/GCMC	W	nm	Pore width (slit shape)
	r_p	nm	Pore radius (cylindrical or cage shape)
	d_p	nm	Pore diameter (cylindrical or cage shape)
	d_s	nm	Adsorbent atom diameter
	V_p	$cm^3\ g^{-1}$	Pore volume
	dV_p	$cm^3\ g^{-1}$	Differential pore volume
	dV_p / dW	$cm^3\ g^{-1}\ nm^{-1}$	Pore area distribution (slit shape)
	$dV_p / d\log W$	$cm^3\ g^{-1}$	Pore volume distribution (slit shape)
	dV_p / dr_p	$cm^3\ g^{-1}\ nm^{-1}$	Pore area distribution (cylindrical or cage shape)
	$dV_p / d\log r_p$	$cm^3\ g^{-1}$	Pore volume distribution (cylindrical or cage shape)
	dV_p / dd_p	$cm^3\ g^{-1}\ nm^{-1}$	Pore area distribution (cylindrical or cage shape)
	$dV_p / d\log d_p$	$cm^3\ g^{-1}$	Pore volume distribution (cylindrical or cage shape)
	ΣV_p	$cm^3\ g^{-1}$	Cumulative pore volume
	da_p	$m^2\ g^{-1}$	Differential pore area
	da_p / dW	$m^2\ g^{-1}\ nm^{-1}$	Pore length distribution (slit shape)
	$da_p / d\log W$	$m^2\ g^{-1}$	Pore area distribution (slit shape)
	da_p / dr_p	$m^2\ g^{-1}\ nm^{-1}$	Pore length distribution (cylindrical or cage shape)
	$da_p / d\log r_p$	$m^2\ g^{-1}$	Pore area distribution (cylindrical or cage shape)
	da_p / dd_p	$m^2\ g^{-1}\ nm^{-1}$	Pore length distribution (cylindrical or cage shape)
	$da_p / d\log d_p$	$m^2\ g^{-1}$	Pore area distribution (cylindrical or cage shape)
	Σa_p	$cm^3\ g^{-1}$	Cumulative pore area

Adsorption/desorption isotherm

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, $p(i)$ kPa, the pressure of i-th measurement point is expressed in kPa. X-coordinate value can be calculated as follows.

In case "$p(i) / p_0$" is selected as the x-axis unit:

$$x(i) = p(i) / p_0(i)$$

(Where $p_0\ (i)$ / kPa is saturation vapor pressure of the adsorptive at measurement temperature.)

In case "p / kPa" is selected as the x-axis unit:

$$x(i) = p(i)$$

In case "p / Torr[*1]" is selected as the x-axis unit:

$$x(i) = p(i) / 101.325 \times 760$$

In case "RH / %" is selected as the x-axis unit:

$$x(i) = p(i) / p_0(i) \times 100$$

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 as the Y axis unit:

$$y(i) = v(i)$$

In case "m_a / mg g^{-1} [*3]" is selected as the y-axis unit:

$$y(i) = v(i) / 22414 \times M_g$$

(Where M_g is moleculer weight of adsorptive.)

In case"Γ / molec nm^{-2} [*4]" is selected as the y-axis unit:

$$y(i) = v(i) / 22414 \times 6.022 \times 10^{23} / a_s \times 10^{-18}$$

(Where a_s / m^2 g^{-1} is the specific surface area of adsorbent.)

In case "n_a / mol mol^{-1} [*5]" is selected as the y-axis unit:

$$y(i) = v(\underline{i)\,}/ 22414 \times M_s$$

(Where M_s is moleculer weight of sample.)

In case n_a / mol g^{-1} [*6] is selected as the y-axis unit:

$$y(i) = v(i) / 22414$$

In case wt / % [*7] is selected as the y-axis unit:

$$y(i) = v(i) / 22414 \times M_g \times 100$$

(Where M_g is moleculer weight of adsorptive.)

In case α_s [*8] is selected as the y-axis unit:

$$y(i) = v(i) / (v_{(p/p0 = 0.4)})$$

(Where $v_{(p/p0 = 0.4)}$ is the adosorption volume of the p / p_0 = 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 : 273.15 K, 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 1 mol of adsorbent expressed in mol.

※6 “n_a / mol g^{-1}” is the specific amount adsorbed expressed in mol.

※7 wt “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 V_a ($p / p_0 = 0.4$)

Operation

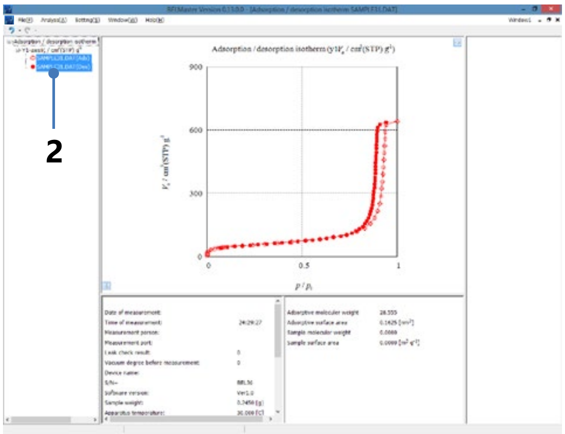
Operation of analysis software

1 Select “Analysis(A)” and then “adsorption/desorption isotherm” from the analysis window menu.

→ Operation P.28 “Open file”

2 An adsorption/desorption isotherm is displayed as shown right.

- For details about how to read the data, see “Reading in analysis data” on P. 28
- “Ads” next to a data name means that it is data from an adsorption branch and “Des” next to a data name means that it is desorption branch.

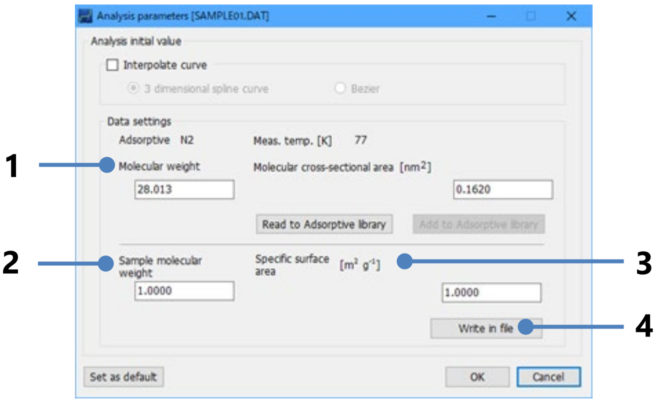


About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters setting(A)” from the analysis window menu. “Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



Analysis parameters [SAMPLE01.DAT]

Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Data settings

Adsorptive N2

Meas. temp. [K] 77

Molecular weight: 28.013

Molecular cross-sectional area [nm2]: 0.1620

Sample molecular weight: 1.0000

Specific surface area [m² g⁻¹]: 1.0000

1	When “m_a / mg g^{-1}” is selected as the Y axis unit in “Y axis display settings”, this value must be entered.
2	When “Γ / molec nm^{-2}” is selected as the Y axis unit in “Y axis display settings”, this value must be entered.
3	When “n_a / mol mol^{-1}” is selected as the Y axis unit in “Y axis display settings”, this value must be entered.
4	The values of sample molecular weight and specific surface area are overwriten in .DAT file. • Use this function only if you analyze .DAT file.

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

- For data including saturation vapor pressure is 0, relatice pressure (p / p_0) and relative humidity (RH / %) are not be able to be selected. (Measure data which adsorption temperature exceeds the critical point of adsorptive could be obtained 0 as the saturation vapor pressure.)

→ About the meanings of each unit P.69 “Description”

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

→ About the meanings of each unit P.69 “Description”

Adsorption rate analysis

Description

Adsorption rate under isothermal conditions can be classified into the following three processes: [1)]

(1) Diffusion rate via adsorbent particle surface fluid film (Fluid film diffusion)

(2) Diffusion rate into inside of adsorbent particles (Pore diffusion)

(3) Adsorption rate on adsorbent particle surface (Surface adsorption)

In normal physical adsorption, adsorption rate of (3) is high, and there is equilibrium state between adsorbent and adsorbate. Therefore, inclusive adsorption rate is determined by (1) and (2).

Fluid film diffusion

In adsorption process, adsorbate molecules pass through the film on the outer surface of adsorbent particles. After adsorbate molecules reach the surface of adsorbent particles, they adhere to the surface of pores in the particles. Therefore, a change in density by distance close to solid phase (adsorbent particles) in gas phase (fluid phase) can be considered by using the model given in Fig. 1. For diffusion via the fluid film, relation of particle – fluid speed can be expressed by film thickness and diffusion coefficient as shown in Equation (1).

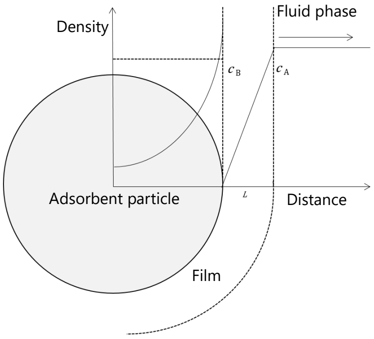


Fig. 1 Distribution of density in direction of adsorbate diffusion

Film thickness will change depending on conditions of fluid velocity, particle size and adsorbate molecular weight, which is defined by film mass transfer coefficient.[1)]

$$\rho_\mathrm{s}\frac{\partial \bar{q}_t}{\partial t} = k_\mathrm{s} a_\mathrm{p}(c_\mathrm{A} - c_\mathrm{B}) \tag{1}$$

$$k_\mathrm{s} = D_\mathrm{AB} / L \tag{2}$$

ρ_s: Adsorbent particle density [kg / m^3], $\bar{q}$: Average adsorption amount [mol / kg], k_s: Film mass transfer coefficient [m / s]

a_p: Outer specific surface area of particle [m^2 / m^3], c_A: Fluid phase density [mol / m^3], c_B: Density on particle outer surface [mol / m^3]

D_AB: Molecule diffusion coefficient [m^2 / s], L: Film thickness [m]

Generally, according to progress of adsorption measurement, rate-determining step shifts from film diffusion to pore diffusion, while density c_B on adsorbent particle surface also changes. In most cases, approximation of linear driving force (LDF) is executed, in which driving force is regarded as $c_\mathrm{A} - c_\mathrm{B}^*$ by using virtual fluid density c^* for average adsorption amount. Thus, adsorption rate is expressed by the following equation. [2)]

$$\rho_\mathrm{s}\frac{\mathrm{d}\bar{q}_\mathrm{t}}{\mathrm{d}t} = k_\mathrm{s} a_\mathrm{p}(c_\mathrm{A} - c_\mathrm{B}^*) \tag{3}$$

Pore diffusion[3~4)]

With pore diffusion in adsorbent particles, collision between molecules is dominant (molecular diffusion) when the pore diameter is large. If the pore diameter is small, collision against pore wall is dominant (Knudsen diffusion). (Fig. 2)

Knudsen diffusion rate depends on pore diameter and adsorbate molecular weight, which is expressed by Equation (4).

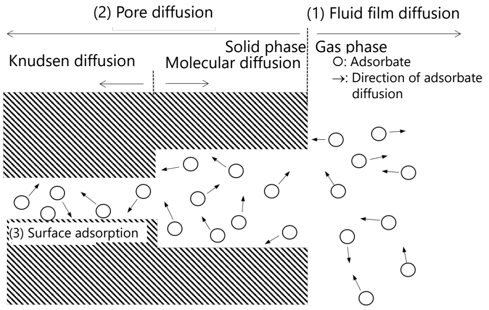


Fig. 2 Knudsen diffusion and molecular diffusion in pore

$$D_{\mathrm{k}} = \frac{4}{3} r \sqrt{\frac{2\,R\,T}{\pi\,M_{\mathrm{A}}}} \tag{4}$$

D_{k}: Knudsen diffusion coefficient $[\mathrm{m}^2 / \mathrm{s}]$, r: Pore radius [m]

R: Gas constant $[\mathrm{m}^2\ \mathrm{kg} / \mathrm{s}^2\ \mathrm{K\ mol}]$, T: Temperature [K], M_{A}: Adsorbate molecular weight [kg / mol]

With actual adsorbent, pore diameter distribution is considered. Therefore, parallel diffusion occurs (molecular diffusion and Knudsen diffusion), which is expressed by Equation (5).

$$\frac{1}{D_0} = \frac{1}{D_{\mathrm{m}}} + \frac{1}{D_{\mathrm{k}}} \tag{5}$$

D_0: Pore diffusion coefficient $[\mathrm{m}^2 / \mathrm{s}]$、$D_{\mathrm{m}}$: Molecular diffusion coefficient $[\mathrm{m}^2 / \mathrm{s}]$

When overall pore diffusion resistance (1 / D_0) is small, molecular diffusion is dominant. If the diffusion resistance is large, Knudsen diffusion is dominant. In the middle range, both molecular diffusion and Knudsen diffusion occur.[4)]

Analysis solution considering LDF approximation

Obtain a solution of analysis of overall mass transfer coefficient for diffusion between adsorbent particles and diffusion in pores (molecular diffusion, Knudsen diffusion and pore surface diffusion). Through LDF approximation using Equation (3), density (*C*) is divided by adsorbent particle density (ρ_s), which is expressed by Equation (6):

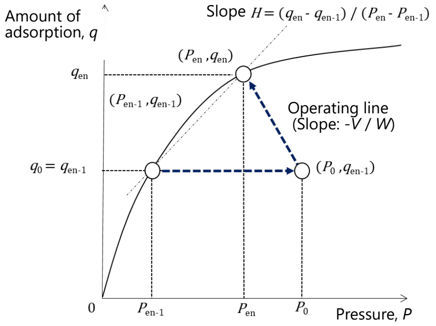


Fig. 3 Relationship between adsorption isotherm and batch adsorbing operation

$$\frac{\mathrm{d}\bar{q}_{\mathrm{t}}}{\mathrm{d}t} = k_{\mathrm{s}} a_{\mathrm{p}} (q_{\mathrm{A}} - q_{\mathrm{B}}^{*}) \tag{6}$$

With Henry (linear) adsorption equilibrium equation, relationship between amount of adsorption and pressure can be expressed by Equation (7).

$$q^{*} = H\,p \tag{7}$$

H: Equilibrium constant [m^3 / g]、p: Pressure [Pa]

As shown in Fig. 3, adsorption isotherm measurement is half-batch operation. Thus, Equation (8) for batch adsorbing operation is used.

$$W(q - q_0) = V(p_0 - p) \tag{8}$$

W: Mass of adsorbent [g]、V: Fluid volume [m^3]

Equation (9) is derived from Equations (6) to (8).

$$q = \left(\frac{\alpha}{\alpha + 1}\right) H p_0 - \left(\frac{\alpha}{\alpha + 1}\right) H p_0 \exp\left(-\left(\frac{\alpha + 1}{\alpha}\right) k_{\mathrm{s}}\, a_{\mathrm{p}}\, t\right) \tag{9}$$

$\alpha = \dfrac{V}{W\,H}$: Separtion factor、t: Time [s]

As separation factor α becomes smaller, it indicates that adsorbate shifts from fluid phase to solid phase.

By solving Equation (9) for p / p_0, the following equation is obtained:

$$\frac{p}{p_0} = 1 - \left(\frac{1}{\alpha + 1}\right)\left[1 - \exp\left(-\left(\frac{\alpha + 1}{\alpha}\right) k_{\mathrm{s}} a_{\mathrm{p}} t\right)\right] \tag{10}$$

Equation (11) is obtained by solving the equation for relationship between amount of adsorption and pressure before and after adsorption measurement at the *n*-th point.

$$\frac{p - p_{\mathrm{en}}}{p_0 - p_{\mathrm{en}}} = 1 - \left(\frac{p_0 - p_{\mathrm{en-1}}}{p_0 - p_{\mathrm{en}}}\right)\left(\frac{1}{\alpha + 1}\right)\left[1 - \exp\left(-\left(\frac{\alpha + 1}{\alpha}\right) k_{\mathrm{s}} a_{\mathrm{p}} t\right)\right] \tag{11}$$

With the ideal gas state Equation (*P* = *cRT*), Equation (11) is transformed to the following equation, from which solution of analysis considering LDF approximation can be obtained.

$$\frac{C - C_{\mathrm{en}}}{C_0 - C_{\mathrm{en}}} = 1 - \left(\frac{C_0 - C_{\mathrm{en-1}}}{C_0 - C_{\mathrm{en}}}\right)\left(\frac{1}{\alpha + 1}\right)\left[1 - \exp\left(-\left(\frac{\alpha + 1}{\alpha}\right) k_{\mathrm{s}} a_{\mathrm{p}} t\right)\right] \tag{12}$$

Wherein, relationship between each pressure value and density *C* is expressed by Equations (13) to (15), respectively.

$$C_0 = \frac{p_{\mathrm{Vs\,in}} V_{\mathrm{s}} + p_{\mathrm{Vd\,en-1}} V_{\mathrm{d}}}{V_{\mathrm{s}} + V_{d}} \tag{13}$$

$$C = p_{\mathrm{Vs\,t}} \tag{14}$$

$$C_{\mathrm{en}} = p_{\mathrm{Vd\,en}} \tag{15}$$

Wherein, $p_{\mathrm{Vma\,in}}$ is pressure in V_{ma} part at the timing of dosing gas, $p_{\mathrm{Vfs\,e\,n-1}}$ is equilibrium pressure in V_{fs} part,
$p_{\mathrm{Vma\,t}}$ is pressure in V_{ma} part at each time, $p_{\mathrm{Vfs\,en}}$ is pressure in V_{fs} part at equilibrium,
V_{ma} is manifold volume, V_{fs} is free space volume.

Analysis solution considering pore diffusion

Adsorption rate considering diffusion in pores is expressed by Equation (16) (on the assumption of spherical particles).

$$\frac{\partial q}{\partial t} = D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{16}$$

Boundary condition: When $r = R$, $q = q_{0n}$.

When Equations (7) and (8) are applied to Equation (16)

$$\frac{p}{p_0} = 1 - \left(\frac{1}{\alpha+1}\right)\left[1 - \sum_{n=1}^{\infty}\frac{6\alpha(\alpha+1)\exp(-q_n^2\tau_s)}{9+9\alpha+q_n^2\alpha^2}\right] \tag{17}$$

Equation (17) is called "Crank equation". When Equation (17) is solved as with Equation (11):

$$\frac{p-p_{en}}{p_0-p_{en}} = 1 - \left(\frac{p_0-p_{en-1}}{p_0-p_{en}}\right)\left(\frac{1}{\alpha+1}\right)\left[1 - \sum_{n=1}^{\infty}\frac{6\alpha(\alpha+1)\exp(-q_n^2\tau_s)}{9+9\alpha+q_n^2\alpha^2}\right] \tag{18}$$

With gas state Equation ($P = cRT$), Equation (18) is expressed as the following equation, from which solution of analysis considering pore diffusion can be obtained.

$$\frac{C-C_{en}}{C_0-C_{en}} = 1 - \left(\frac{C_0-C_{en-1}}{C_0-C_{en}}\right)\left(\frac{1}{\alpha+1}\right)\left[1 - \sum_{n=1}^{\infty}\frac{6\alpha(\alpha+1)\exp(-q_n^2\tau_s)}{9+9\alpha+q_n^2\alpha^2}\right] \tag{19}$$

$$\text{Wherein,}\quad \tau_s = \frac{D_s}{R^2}t\text{、}\quad \tan q_n = \frac{3q_n}{3+\alpha q_n^2}$$

1) Suzuki, M., "Adsorption engineering", Kodansha, pp. 98-100 (1990)
2) Glueckauf, E. "Theory of chromatography", Trans.Faraday Soc, vol51, 1540 (1955).
3) R.T.Yang, "Gas Separation by Adsorption Processes" Imperial College Press, London (1997)
4) Kenji Hashimoto, Koichi Miura, "Kyuuchaku Gijutsu Handbook" *NTS*, pp. 444 – 456 (1993)
5) Kunitaro Kawazoe, "Kyuuchaku niokeru Busshitsu Idou", *Chemical Engineering*, vol29, 404 (1965)
6) Crank,J, "The Mathematics of Diffusion", Oxford Science Publications (1975)
7) "Kyuuchaku Bunnrizai no Sekkei, Seinou Hyouka to Atarashii Ouyou", *Technical Information Association*, pp. 318 – 327 (2015)

Operation

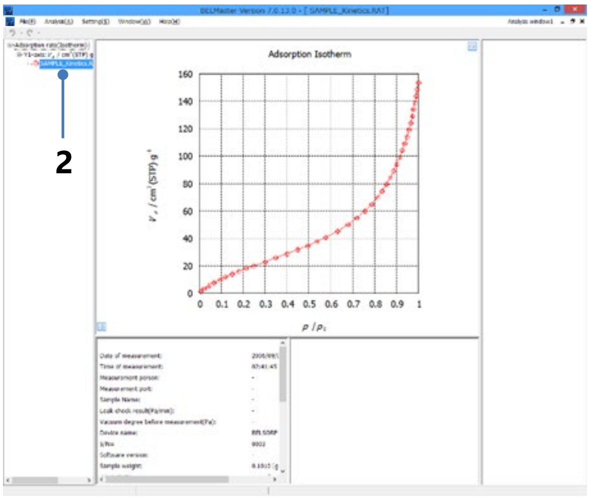
Operation of analysis software

1 Select “Analysis(A)” and then “Adsorption rate analysis” from the analysis window menu.

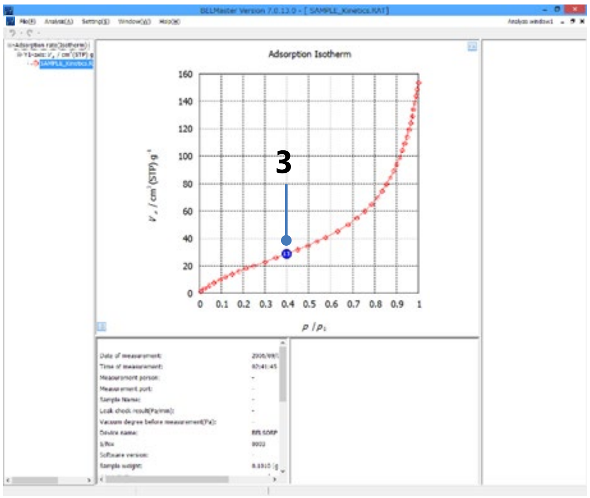
→ Operation P.28 “Open file”

2 An adsorption isotherm is displayed, as shown on the right.

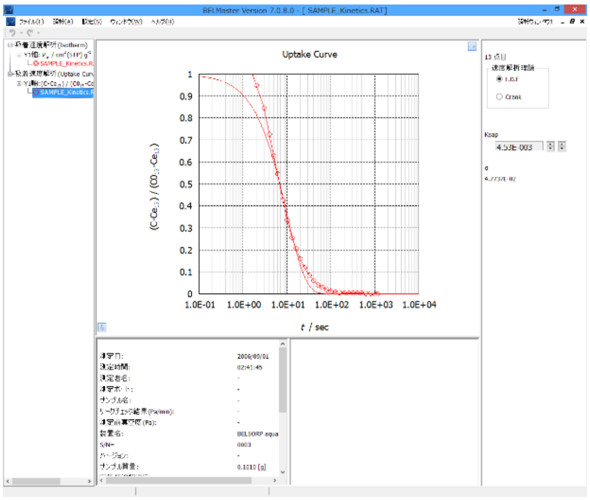
- For details about how to read the data, see “Reading in analysis data” on P. 28
- Only .RAT or .NRAT file can be read.



3 Click a desired analysis point on the displayed adsorption isotherm. A blue circle appears to indicate a data No.



4 Double-clicking a desired analysis point displays an adsorption rate analysis graph which shows change in density in gas phase relative to time. The marker indicates a measured value. The solid line indicates a model curve.
In the overwriting case, the data excluding the active data is displayed with the gray curve.



5 Select "L.D.F" or "Crank" as rate analysis theory according to the purpose of analysis.
With L.D.F. approximation, mass transfer coefficient ($K_s\alpha_p$) can be obtained. With Crank equation, surface diffusion coefficient (D_s / R^2) can be obtained.


Model
● L.D.F
○ Crank

6 Adjust each analysis theory parameter so that the model curve (solid line) is most exactly fit on the measurement point (marker).
In initial status, model fitting is executed so as to meet $\frac{C-C_{en}}{C_{on}-C_{en}} = 0.5$ (measured value).

➢ X axis display settings in displaying adsorption isotherm

Select "Settings(S)" → "X axis display settings(X)" to select desired unit of X axis.

→ About the meanings of each unit P.69 "Description"

➢ Y axis display settings in displaying adsorption isotherm

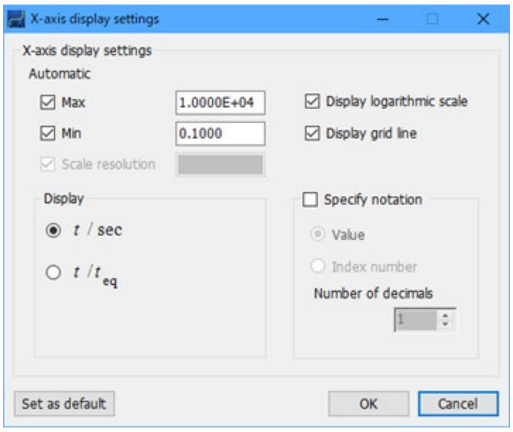
Select "Settings(S)" → "Y axis display settings(Y)" to select desired unit of X axis.

→ About the meanings of each unit P.69 "Description"

➢ X axis display settings in displaying uptake curve

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

・ *t* / sec	Display time (seconds) as horizontal axis.
・ *t* / t_{eq}	Display standardized dimensionless time as horizontal axis.



☑ Max 1.0000E+04
☑ Min 0.1000
☑ Scale resolution
☑ Display logarithmic scale
☑ Display grid line
● *t* / sec
○ *t* / t_{eq}
☐ Specify notation
● Value
○ Index number
Number of decimals 1

➢ Y axis display settings in displaying uptake curve

Select “Settings(S)” → “Y axis display settings(Y)” to select desired setting of Y axis.

PCT curve

Description

PCT (Pressure-Composition-Temperature) curve 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 as the x-axis unit:

$$x(i) = 2 \times v(i) \times M_{metal} / 22414 \qquad \text{(Where } M_{\mathrm{metal}} \text{ is molecular weight of metal)}$$

When "*wt %* " *2 is selected as the x-axis unit:

$$x(i) = v(i) / 22414 \times M_g \times 100 \qquad \text{(Where } M_{\mathrm{g}} \text{ is moleculer weight of adsorptive)}$$

When "cm^3 (STP) g^{-1}" *3 is selected as the x-axis unit:

$$x(i) = v(i)$$

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 as the y-axis unit:

$$y(i) = p(\mathrm{i})$$

When "*p* / MPa" is selected as the y-axis unit:

$$y(i) = p(i) \times 1000$$

When "*p* / bar" is selected as the y-axis unit:

$$y(i) = p(i) / 1000$$

※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 273.15 K and 101.325 kPa, converted from amount of adsorption by 1 g of sample (metal).

Operation

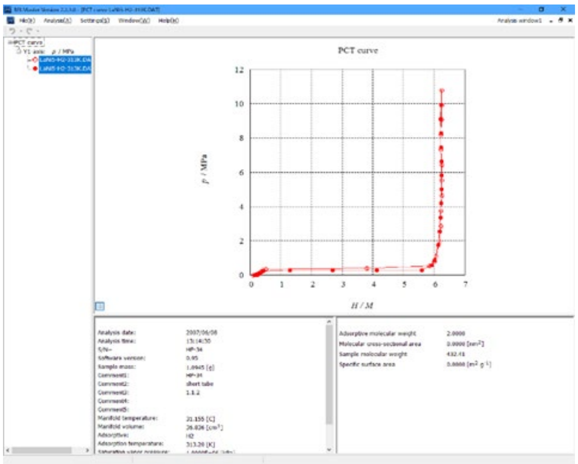
Operation of analysis software

1 Select “Analysis(A)” and then “PCT curve” from the analysis window menu.

→ Operation P.28 “Open file”

2 A PCT curve is displayed as shown right.

- For details about how to read the data, see “Reading in analysis data” on P. 28
- While displaying the PCT curve, the right sub window is not displayed.

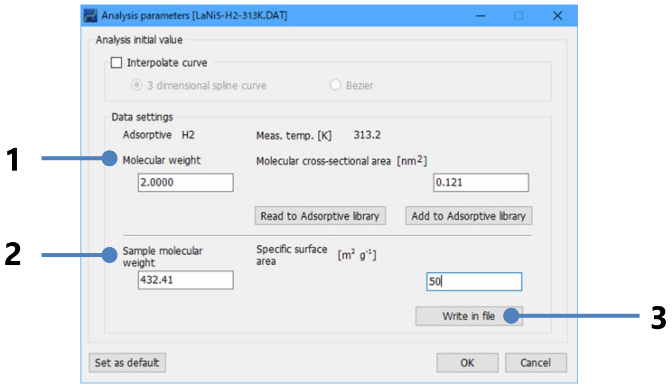


About analysis parameters settings

➢ Analysis parameters settings

Select "Settings(S)" and then "Analysis parameters setting(A)" from the analysis window menu. "Analysis parameters" window shown below will appear. Change the settings as needed.

- For details about items not described here, see "Analysis parameters setting", on P.37


Analysis parameters [LaNi5-H2-313K.DAT]

Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Data settings

Adsorptive H2

Meas. temp. [K] 313.2

Molecular weight 2.0000

Molecular cross-sectional area [nm2] 0.121

Sample molecular weight 432.41

Specific surface area [m^2 g^{-1}] 50

1	This parameter is required when "*wt %*" is selected for the unit of the X axis in "X-axis display settings".
2	This parameter is required when"*H/M*" is selected for the unit of the X axis in "X-axis display settings".
3	The values of sample molecular weight and specific surface area are overwriten in .DAT file. • Use this function only if you analyze .DAT file.

➢ X axis display settings

Select "Settings(S)" → "X axis display settings(X)" to select desired unit of X axis.

→ About the meanings of each unit "Description" P.80

➢ Y axis display settings

Select "Settings(S)" → "Y axis display settings(Y)" to select desired unit of Y axis.

→ About the meanings of each unit "Description" P.80

BET analysis

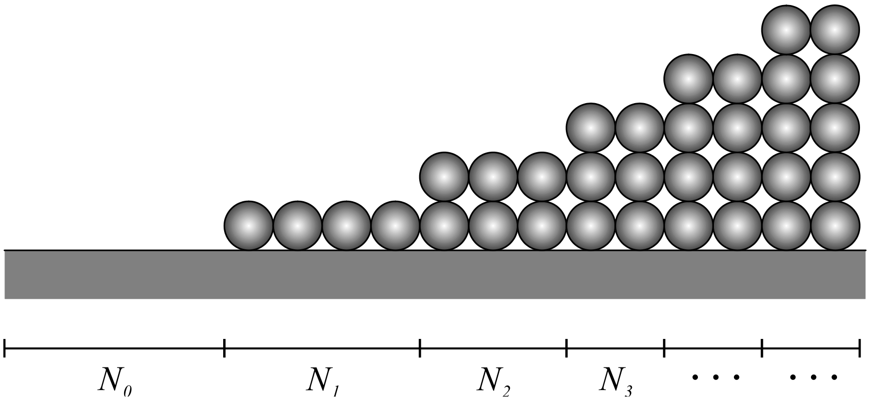
Description

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 amount of adsorbed gas, from which we can calculate the surface area of adsorbent.

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 adsorate (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 and the number of the adsorptive (i.e. the pressure for the equilibrium state). 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 (1) is obtained.

$$a_1\, p\, N_0 = b_1\, N_1 \exp\left(-\frac{E_1}{R\,T}\right) \tag{1}$$

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:

$$a_1\, p\, N_0 \;+\; b_2\, N_2 \exp\left(-\frac{E_2}{R\,T}\right) = a_2\, p\, N_1 + b_1\, N_1 \exp\left(-\frac{E_1}{R\,T}\right) \tag{2}$$

Equation (3) is obtained by substituting Equation (1) into Equation (2),

$$a_2\, p\, N_1 \;= b_2\, N_2 \exp\left(-\frac{E_2}{R\,T}\right) \tag{3}$$

Extending the same argument to the *i*-th layer (N_i = constant), Equation (4) can be derived.

$$a_{\mathrm{i}}\, p\, N_{i-1} \;= b_i\, N_i \exp\left(-\frac{E_i}{R\,T}\right) \tag{4}$$

Equation (4) is tranformed into Equation (5).

$$N_i \;= \frac{a_i}{b_i}\, p\, N_{i-1} \exp\left(\frac{E_i}{R\,T}\right) \tag{5}$$

Equation (6) may be obtained if the adsorption behavior of gas is same for higher than the second layer,

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \varLambda \;= \frac{b_i}{a_i} = g \tag{6}$$

From both of Equation (6) and hypothesis 3), Equation (5) can be transformed into Equation (7) and Equation (8) when $i \geq 2$:

$$N_i \;= \frac{p}{g}\, N_{i-1} \exp\left(\frac{E_{\mathrm{L}}}{R\,T}\right) \tag{7}$$

Here, we define x as follows:

$$N_{\mathrm{i}-1} \;= \frac{p}{g}\, N_{\mathrm{i}-2} \exp\left(\frac{E_{\mathrm{L}}}{R\,T}\right) \tag{8}$$

By inserting Equation (8) into Equation (7), Equation (9) is obtained:

$$N_i \;= x^2\, N_{i-2} \tag{9}$$

Wherein,

$$x \;= \frac{p}{g} \exp\left(\frac{E_{\mathrm{L}}}{R\,T}\right) \tag{10}$$

By repeating the above operation, Equation (12) is obtained when $i \geq 2$:

$$N_i \;= x^{i-1}\, N_1 \tag{11}$$

From equations (1) and (11),

$$N_i \;= \frac{a_1}{b_1}\, x^{i-1}\, p\, N_0 \exp\left(\frac{E_1}{R\,T}\right) = \;x^i\, N_0\, \frac{a_1}{b_1}\, g \exp\left(\frac{E_1 - E_{\mathrm{L}}}{R\,T}\right) = C\, x^i\, N_0 \tag{12}$$

Wherein,

$$C = \frac{a_1}{b_1} g \exp\left(\frac{E_i - E_\mathrm{L}}{R\,T}\right) \tag{13}$$

The total number of sites (N_s) and the total number of adsorption molecules (N_a) are expressed as follows:

$$N_\mathrm{s} = \sum_{i=0}^{\infty} N_i = N_0 + \sum_{i=1}^{\infty} N_i \tag{14}$$

$$N_\mathrm{a} = \sum_{i=0}^{\infty} i\,N_i = \sum_{i=1}^{\infty} i\,N_i \tag{15}$$

When the amount of adsorption is expressed as V_a and the amount of monomolecular layer adsorption is expressed as V_m,

$$\frac{N_\mathrm{a}}{N_\mathrm{s}} = \frac{V_\mathrm{a}}{V_\mathrm{m}} \tag{16}$$

From Equations (12) and (16),

$$\frac{V_\mathrm{a}}{V_\mathrm{m}} = \frac{\sum_{i=1}^{\infty} i\,N_i}{N_0 + \sum_{i=1}^{\infty} N_i} = \frac{C\,N_0 \sum_{i=1}^{\infty} i\,x^i}{N_0 + C\,N_0 \sum_{i=1}^{\infty} x^i} \tag{17}$$

Sum of progression of denominator and numerator is obtained with the following equation each:

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} \tag{18}$$

$$\sum_{i=1}^{\infty} i\,x^i = x\frac{\mathrm{d}}{\mathrm{d}x}\sum_{i=1}^{\infty} x^i = x\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{x}{1-x}\right) = \frac{x}{(1-x)^2} \tag{19}$$

Therefore, Equation (17) is expressed as follows:

$$\frac{V_\mathrm{a}}{V_\mathrm{m}} = \frac{C\,x}{(1-x)(1-x+Cx)} \tag{20}$$

At saturation vapor pressure p_0 of adsorbate, condensation occurs. Because $V = \infty$, $x = 1$ based on Equation (20).

When $x = 1$ and $p = p_0$ in Equation (10), the following equation is obtained.

$$\frac{p_0}{g} \exp\left(\frac{E_\mathrm{L}}{R\,T}\right) = 1 \tag{21}$$

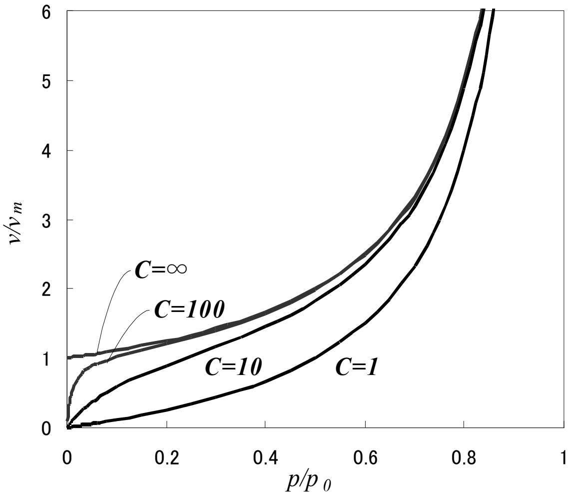
From Equations (10) and (21),

$$x = \frac{p}{p_0} \tag{22}$$

Therefore, the following equation is derived from Equation (20).

$$V_\mathrm{a} = \frac{V_\mathrm{m}\,C\,p}{(p_0 - p)\left[1 + (C-1)\left(\frac{p}{p_0}\right)\right]} \tag{23}$$

This equation is called "BET equation", which expresses adsorption isotherm. When *C* is large (amount of adsorption heat is large), the isotherm is raised in a low-pressure range. When *C* is small (amount of adsorption heat is small), the adsorption amount in a low-pressure range becomes small and the shape of isotherm is similar to isotherm of Type III. Also, in a low-pressure range, it becomes equal to Henry equation as with Langmuir equation.



Equation (23) can be transformed as follows:

$$\frac{p}{V_a\,(p_0 - p)} = \frac{1}{V_m\,C} + \frac{C-1}{V_m\,C}\,\frac{p}{p_0} \tag{24}$$

It is evident from Equation (24) 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 and C) of the BET equation can be calculated using Equations (25) and (26) and the specific surface area is obtained from amount of monomolecular layer:

$$V_m = \frac{1}{s + i} \tag{25}$$

$$C = \frac{s}{i} + 1 \tag{26}$$

C reflects the heat of adsorption in the first layer as shown Equation (13). The molecules in gas phase form on the surface of adsorbent and the entropy of the whole system decreases. To proceed adsorption phenomenon, the increase of enthalpy which is larger than the decrease of entropy is needed. In other words, adsorption phenomenon accompany with exothermic phenomenon and the value of *C* must be positive.

In many adsorbents, the BET plot gives the good linear line in relative pressure range 0.05 to 0.35, but it deviates from the linear line in low or high relative pressure range (especially, porous adsorbents). The deviation in low relative pressure range is derived from the specific adsorption due to heterogeneous surface of adsorbent. And, the deviation in high relative pressure range is derived from supposing that the amount adsorbed at the saturation vapor pressure is ∞ (in fact, the amont adsorbed has limit). And, the model which the adsorption layers in various layers number exist at the same time is said to be not realistic from the property of liquid.

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 (27)) 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 parameters equation is not frequently used because of complexity.

$$V_\mathrm{a} = \frac{V_\mathrm{m}\, C\, x}{(1-x)} \left[\frac{1-\ (n+1)\, x^{n} + n x^{n+1}}{1+\ (C-1)\, x - C x^{n+1}} \right] \tag{27}$$

Equation (27) is reduced to Lamgmuir equation when $n = 1$. A variety of modified BET equation are reported, however, Equation (23) is the most commonly used because of its simplicity.

[Note] There is a criticism that it is inappropriate to apply the BET theory to Type I isotherm. In this case, to determine the end point, the BET range limit is needed. BET range limit is the relative pressure p / p_0 having the maximum value when the relative pressure p / p_0 is plotted on the X axis and $V_\mathrm{a}\,(p_0 - p)$ is plotted on the Y axis. To determine the starting point, use caution about the following three points: [1] BET parameter 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 $1 / V_\mathrm{m}C$, which is so small that it can be regarded as zero. Thus, the Equation (24) is expressed as follows:

$$\frac{p}{V_\mathrm{a}\,(p_0 - p)} = \frac{C-1}{V_\mathrm{m}\, C}\, \frac{p}{p_0} \tag{28}$$

The following equation is derived by simplifying the Equation (28):

$$V_\mathrm{m} = V_\mathrm{a} \left(1 - \frac{p}{p_0}\right) \tag{29}$$

Monolayer amount V_m can be obtained by measuring an adsorption amount V_a at arbitrary equilibrium relative pressure p / p_0. Thus, V_m can be determined based on measurement of one point at equilibrium relative pressure p / p_0 (generally, in a relative pressure range of 0.2 to 0.3). (BET single point method)

With this analysis software, prepare BET-plot first, and the select “Single point method” and enter the “Relative pressure” in the analysis parameters window (Refer to P. 90). By plotting a line between two points (origin (0) and the selected point), the software calculates slope s of the line, and determines an amount of monomolecular adsorption V_m, and calculates a specific 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 parameters” settings is calculated by linear interpolation to adsorption data. Then interporated value, V_p [cm^3 g^{-1}] is converted to the volume liquid state as Equation (30). (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.)

$$V_\mathrm{p} = \frac{V\, M_\mathrm{a}}{22414 \times \rho_\mathrm{a}} \tag{30}$$

where M_a is molecular weight and ρ_a is adsorbate liquid density. Mean pore diameter of pore can be obtained as follows by using V_p and $a_{s,BET}$, the BET specific surface area using Equation (31) – (33).

In the case of slit like pore

$$d_\mathrm{p} = \frac{2\, V_\mathrm{p}}{a_\mathrm{s,BET}} \times 10^3 \tag{31}$$

In the case of cylindrical like pore (BELMaster ver. 7.3.2.0 or earlier software calculates as cylindrical like pore)

$$d_\mathrm{p} = \frac{4\, V_\mathrm{p}}{a_\mathrm{s,BET}} \times 10^3 \tag{32}$$

In the case of cage like pore

$$d_\mathrm{p} = \frac{6\, V_\mathrm{p}}{a_\mathrm{s,BET}} \times 10^3 \tag{33}$$

Mean particle size is calculated as follows.

$$l = \frac{6}{\rho_\mathrm{s} \times a_\mathrm{s,BET}} \times 10^3 \tag{34}$$

where ρ_s is density of adsorbent.

≪Reference≫

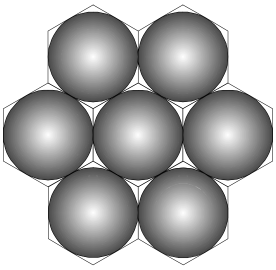
- “Adsorption of Gases in Multimolecular Layers”, Stephen Brunauer, P. H. Emmett and Edward Teller, *J. Am. Chem. Soc.*, **60**, 309 （1938）.
- ISO9277

Determination of surface area from monolayer amount

Specific surface area of adsorbent (a_s) can be calculated by Equation (33).

$$a_{\mathrm{s,BET}} = \frac{V_{\mathrm{m}}}{22414} \times L \times \sigma \tag{33}$$

where V_m is monolayer amount, 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_a and the adsorbate liquid density ρ_a.

$$\sigma = 2\sqrt{3}\left(\frac{M_{\mathrm{a}}}{4\sqrt{2}\,L\,\rho_{\mathrm{a}}}\right)^{\frac{2}{3}} \tag{34}$$

In case of the nitrogen adsorption at liquid nitrogen temperature, σ (N_2) = 0.162 nm^2 (M_a = 28.0, ρ_a = 0.808 g cm^{-3}) can be calculated from Equation (34). σ (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 (e.g. oxide or graphite), the different value of σ (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 (34), 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 σ (N_2) = 0.162 nm^2 [*ref.* A. L. McClellan, and H. F. Harnsberger, *J. Colloid Interface Sci.*, **23**, 577(1967).].

Thermodynamics of gas adsorption

It is widely known that heat generation is associated with gas adsorption process generally. The relation between gas adsorption and thermodynamics is given by the Equation (35).

$$\Delta G_{\mathrm{ad}} = \Delta H_{\mathrm{ad}} - T\Delta S_{\mathrm{ad}} \tag{35}$$

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. Since ΔH_{ad} is negative, it is conduced from the Equation (35) that heat generation is associated with gas adsorption.

Operation

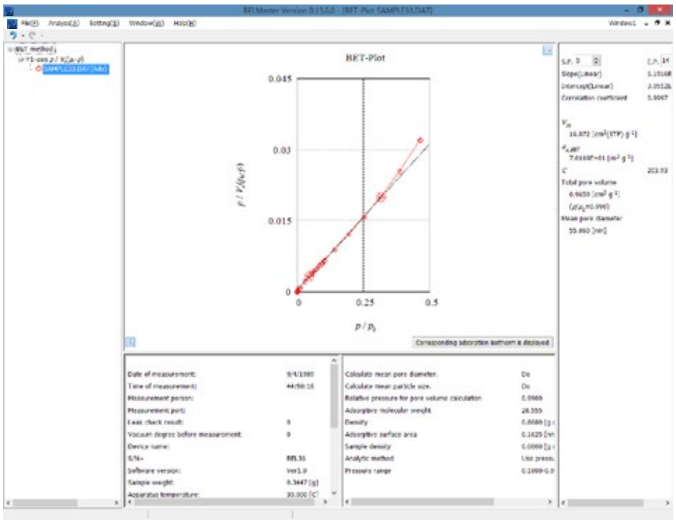
Operation of analysis software

1 Select “Analysis(A)” and then “BET plot” from the analysis window menu.

→ Operation P.28 “Open file”

2 A BET-plot is displayed as shown right. The software automatically draws a straight line.

- The figure on the right is a BET plot of nitrogen adsorption measurements on silica with micropores.



BET-plot of macropore silica

3 Select start and end points within a relative pressure range 0.05-0.30 so that good linearity can be obtained.

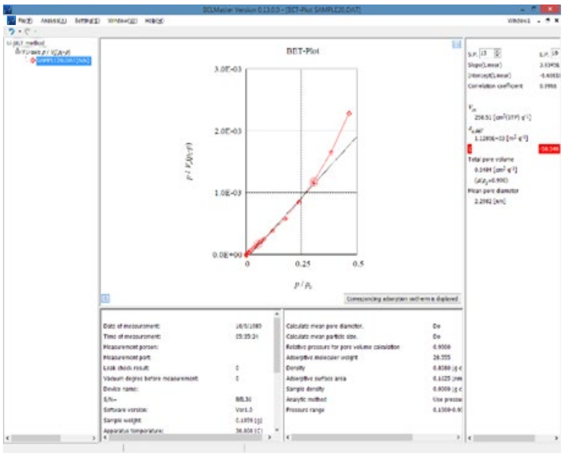
- By default, select 2 points nearest to the pressure range set for “Analysis parameters” to draw an approximate straight line.

4 The monolayer amount (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.

About analysis result

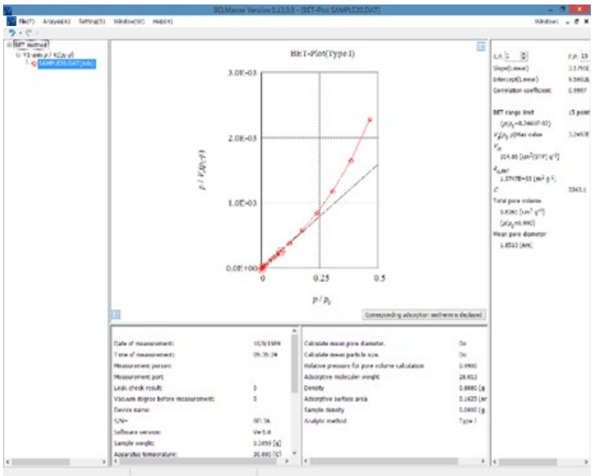
You can obtain a specific surface area ($a_{\mathrm{s,BET}}$ / m^2 g^{-1}) from the monolayer amount (V_{m} / cm^3 g^{-1}) for the adsorption of nitrogen, argon, and krypton. In nitrogen adsorption when C is 100 to 200, it is believed that a reliable specific surface area can be obtained. The specific 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 m^2 g^{-1} obtained from a *t*-plot (P.155).

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.



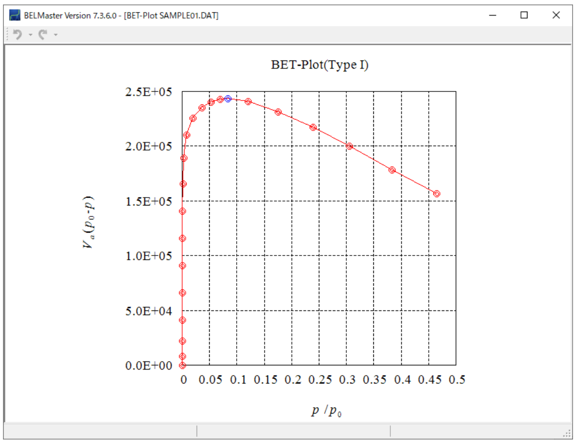
BET-plot of active carbon (p/p_0 = 0.05 to 0.30)

The specific surface area obtained from the BET-plot of this activated carbon is 1370 m^2 g^{-1} (C = 3343). The specific surface area obtained from *t*-plot is 1519 m^2 g^{-1} (P. 157). 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.



BET-plot of active carbon (Type I, ISO9277)

Only when Type I (ISO9277) is selected, the Display volcano plot button appears on the BET-Plot window. Clicking the button will display the Volcano plot (Rouquerol plot) on a separate window, allowing you to see a plot of V_a $(p_0 - p)$.



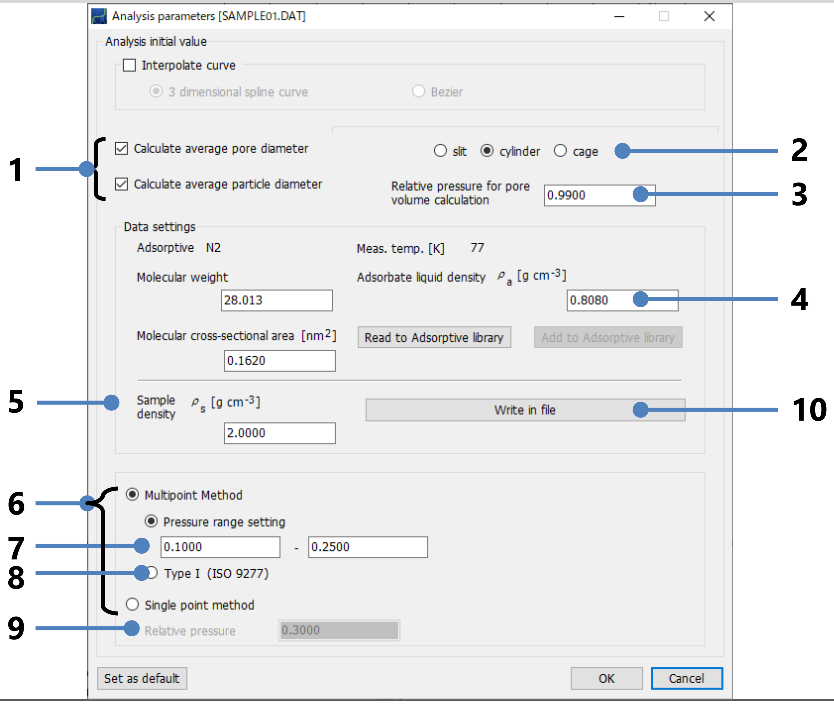
Volcano-plot of active carbon (Type I, ISO9277)

About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters setting(A)” from the analysis window menu. “Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

☑ Calculate average pore diameter ○ slit ● cylinder ○ cage

☑ Calculate average particle diameter

Relative pressure for pore volume calculation 0.9900

Data settings

Adsorptive N2

Meas. temp. [K] 77

Molecular weight 28.013

Adsorbate liquid density ρ_a [g cm^{-3}] 0.8080

Molecular cross-sectional area [nm^2] 0.1620

Sample density ρ_s [g cm^{-3}] 2.0000

● Multipoint Method

● Pressure range setting 0.1000 - 0.2500

○ Type I (ISO 9277)

○ Single point method

Relative pressure 0.3000

1	Select whether or not to calculate the average pore diameter and average particle size.
2	Specifies the pore shape for calculating the average pore diameter. See the equations (31) – (33).
3	Enter a relative pressure to calculate the total pore volume. If the relative pressure at the adsorption end point is lower than the relative pressure entered here, the program will calculate the total pore volume from the adsorption volume at the adsorption end point. Settable range: 0.0001 to 0.9999
4	You must enter this value when you want to calculate the total pore volume and mean pore diameter. Even if you check on “Calculate average pore diameter”, the program will not calculate the total pore volume and average pore diameter unless an adsorbate liquid density is entered.
5	You must enter a value here when you want to calculate the average particle size. Even when you click on the average particle diamter, the program cannot calculate the average particle size unless a sample density is entered.
6	Select either the multipoint or single point method as the analysis method.
7	Enter linear range for analysis in the case of multipoint method.
8	Select this item for Type I adsorption isotherm (for a sample with micropores) to analyze in accordance with ISO 9277.

9	Enter a relative pressure used for single point method analysis.
10	The values of sample density is overwriten in .DAT file. • Use this function only if you analyze .DAT file.

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

➢ Y axis display settings

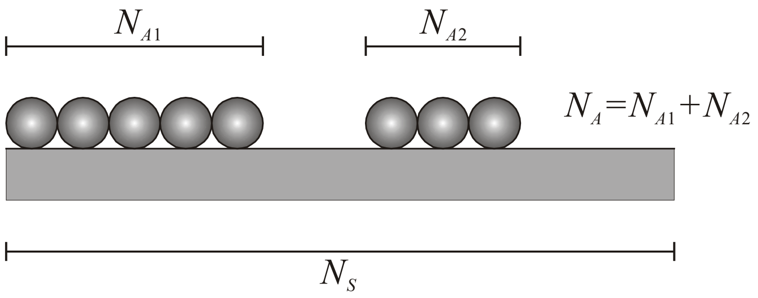
Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

Langmuir plot

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:

$$\theta = \frac{N_{\mathrm{A}}}{N_{\mathrm{S}}} \tag{1}$$

The adsorption rate, v_{a} is proportional to p (Adsorptive pressure) and 1 - θ (bare surface);

$$v_{\mathrm{a}} = k_{\mathrm{a}}\, p\, (1 - \theta) \tag{2}$$

On the other hand, the desorption rate, v_{d} is proportional to θ (Surface coverage);

$$v_{\mathrm{d}} = k_{\mathrm{d}}\, \theta \tag{3}$$

k_{a} and k_{d} in Equations (2) and (3) are the proportional constants.

Under the adsorption equilibrium, the adsorption rate is equal to that of desorption;

$$k_a\, p\, (1 - \theta) = k_{\mathrm{d}}\, \theta \tag{4}$$

Equation (4) is changed into Equation (5),

$$B\, p\, (1 - \theta) = \theta \tag{5}$$

where k_{a} / k_{d} is shown as B. When Equation (5) is solved for θ, Equation (6) is obtained.

$$\theta = \frac{B\, p}{1 + B\, p} \tag{6}$$

Furthermore, Equation (6) is expressed using the monolayer amount, V_{m}. The amount of adsorbed gas at an arbitrary pressure is expressed as follows;

$$V_\mathrm{a} = V_\mathrm{m}\,\theta \tag{7}$$

By putting Equation (7) into Equation (6), we obtain Equation (8), the Langmuir equation.

$$V_\mathrm{a} = \frac{V_\mathrm{m}\,B\,p}{1 + B\,p} \tag{8}$$

If the condition of $1 \gg Bp$ (low pressure range) is satisfied, Equation (8) is transformed to Equation (9);

$$V_\mathrm{a} = V_\mathrm{m}\,B\,p \tag{9}$$

Equation (9) is called Henry equation, where the amount of adsorbed gas is proportional to the adsorptive pressure.

Equation (8) can be converted to Equation (10).

$$\frac{p}{V_\mathrm{a}} = \frac{1}{B\,V_\mathrm{m}} + \frac{p}{V_\mathrm{m}} \tag{10}$$

Equation (10) 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 amount, 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 amount (V_m), the Langmuir constant (B), and the surface area ($a_\mathrm{s,Lang}$) can be calculated by means of the least-square method, and are displayed.

[Notice]:

The Langmuir Equation (8), 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 amount (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 $\mathrm{m}^2\ \mathrm{g}^{-1}$. This value is larger than the maximum surface area, 2,630 $\mathrm{m}^2\ \mathrm{g}^{-1}$, 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. Am. Chem. Soc.*, **38**, 2219 (1916); **40**, 1368 (1918)

Operation

Operation of analysis software

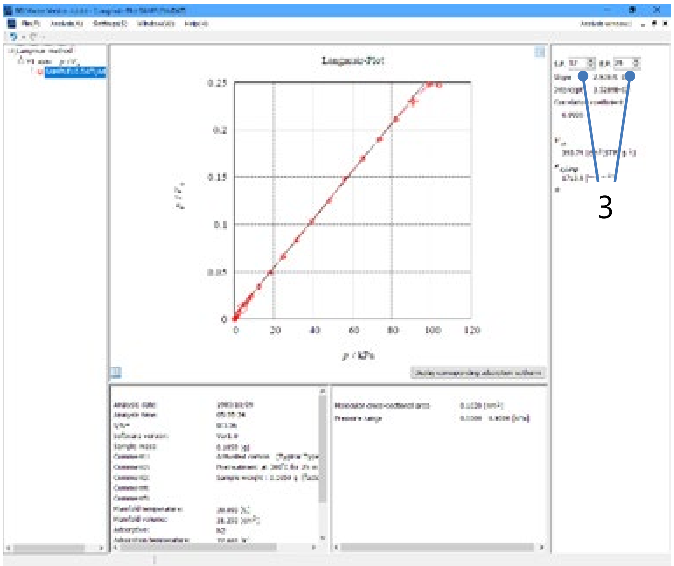
1 Select “Analysis(A)” and then “Langmuir plot” from the analysis window menu.

- The software will execute a Langmuir plot from adsorption data of an isotherm adsorption.

→ Operation P.28 “Open file”

2 A Langmuir-plot is displayed as shown right. The software automatically draws a straight line.

- The default selection is the start point as the minimum data point and the end point as the maximum data point.



3 Select the starting and end points to obtain good linearity.

4 The software obtains the monolayer amount(V_{m} / $\mathrm{cm^3\ g^{-1}}$) and the B value from the slope of the approximate curve and intercept. The software will also display the correlation coefficient of the approximate straight line.

About analysis result

In a chemisorption measurement, the chemisorption amount can be obtained from the monolayer amount (V_{m} / $\mathrm{cm^3(STP)\ g^{-1}}$).

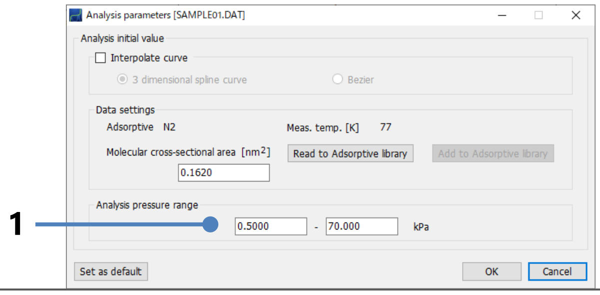
The nitrogen adsorption isotherm on a sample with micropores is shown as type I, and gives good linearity in a Langmuir-plot. However, as described in the [Description], there is a tendency that the specific area obtained may be larger than the actual value. The figure above shows a Langmuir-plot of microporous activated carbon. The specific surface area obtained will be 1,706 $\mathrm{mm^2\ g^{-1}}$ and this is larger than the actual value (1,400 to 1,500 $\mathrm{m^2\ g^{-1}}$, on P. 95).

About analysis parameters settings

➢ Analysis parameters settings

Select “Setting s(S)” and then “Analysis parameters setting(A)” from the analysis window menu. “Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



Analysis parameters [SAMPLE01.DAT]

Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Data settings

Adsorptive N2

Meas. temp. [K] 77

Molecular cross-sectional area [nm^2] 0.1620

Analysis pressure range 0.5000 - 70.000 kPa

1	Enter a linear range for analysis.

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

Freundlich plot

Description

With Langmuir plot, it is assumed that all adsorption sites on an adsorbent surface have equal adsorption energy, or that adsorption heat q is fixed, regardless of surface coverage θ.

On the other hand, with Freundlich plot, it is assumed that all adsorption sites on an adsorbent surface have different adsorption energy, or that adsorption heat q linearly changes depending on surface coverage θ.

$$q = -q_{\mathrm{m}} \ln \theta \tag{1}$$

Wherein, q_{m} indicates adsorption heat at $\theta = \frac{1}{e} = 0.3679$

As per Equations (4) and (5) given in the description of Langmuir plot (P. 95), the following equation is obtained.

$$B = \frac{k_{\mathrm{a}}}{k_{\mathrm{d}}} = \frac{\theta}{p\,(1 - \theta)} \tag{2}$$

When Arrhenius equation is applied to adsorption rate constant k_{a} and desorption rate constant k_{d}, the following two equations are obtained.

$$k_{\mathrm{a}} = a\, e^{-\frac{E_{\mathrm{a}}}{R\,T}} \tag{3}$$

$$k_{\mathrm{d}} = d\, e^{-\frac{E_{\mathrm{d}}}{R\,T}} \tag{4}$$

a, d: constant, E_a: Adsorption energy, E_d: Desorption energy

Therefore, equilibrium constant B can be also expressed as the following equation, by using Equations (3) and (4) constant K_0 and adsorption heat q.

$$B = \frac{k_{\mathrm{a}}}{k_{\mathrm{d}}} = K_0 \exp\left(\frac{q}{R\,T}\right) \tag{5}$$

The following equation is derived from Equations (2) and (5).

$$\frac{\theta}{P\,(1 - \theta)} = K_0 \exp\left(\frac{q}{R\,T}\right) \tag{6}$$

From Equation (1),

$$\frac{\theta}{P\,(1 - \theta)} = K_0 \exp\left(\frac{-q_{\mathrm{m}} \ln \theta}{R\,T}\right) \tag{7}$$

By taking logarithm of both sides, the above equation can be transformed to the following equation:

$$\ln \frac{1}{P} + \ln\left(\frac{\theta}{1 - \theta}\right) = \ln K_0 - \frac{q_{\mathrm{m}}}{R\,T} \ln \theta \tag{8}$$

By rearranging Equation (8), Equation (9) is obtained.

$$\ln\theta + \frac{R\,T}{q_\mathrm{m}}\ln\left(\frac{\theta}{1-\theta}\right) = \frac{R\,T}{q_\mathrm{m}}\ln P + \frac{R\,T}{q_\mathrm{m}}\ln K_0 \tag{9}$$

Wherein, when the coverage is large (nearly 1), $\ln\left(\frac{\theta}{1-\theta}\right)$ is can be ignored because it is asymptotically equal to 0. Therefore,

$$\ln\theta = \frac{R\,T}{q_\mathrm{m}}\ln P + \frac{R\,T}{q_\mathrm{m}}\ln K_0 \tag{10}$$

An equation that indicates correlation between coverage and pressure is obtained.

From Equation (10), correlation between adsorption amount on the vertical axis and pressure on the horizontal axis is linear. Also, amount of monolayer amount V_m can be calculated from the intersection of Freundlich equation at two temperatures close to each other.

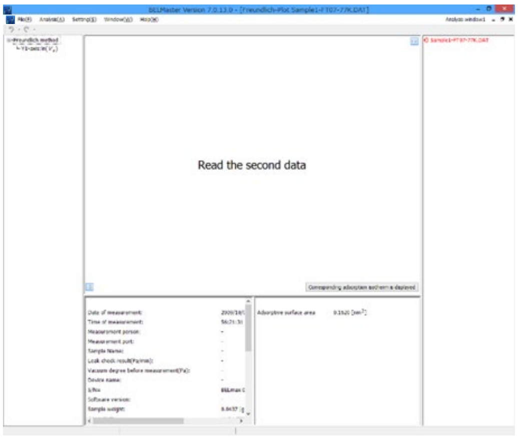
Operation

Operation of analysis software

1 Select “Analysis(A)” and then “Freundlich plot” from the analysis window menu.

→ Operation P.28 “Open file”

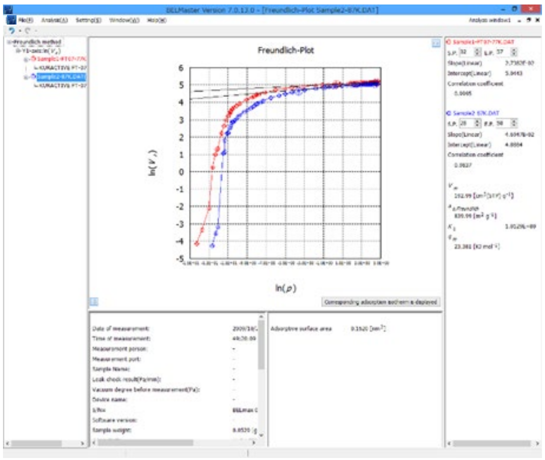
2 After the first data is read, a message appears, prompting you to read the second data.



Read the second data

3 Select “File (F)” → “Overlay” in the analysis window menu, and read the second data, or select “Overlay” from the menu displayed by right-clicking, and read the second data. Also, data can be added by drag & drop operation.

4 Determine a monolayer amount based on these two pieces of data.



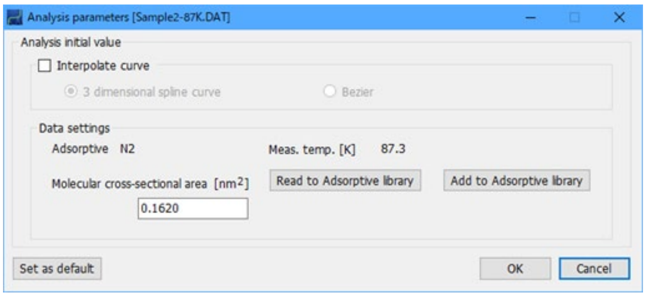
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



☐ Interpolate curve

● 3 dimensional spline curve　○ Bezier

Adsorptive　N2

Meas. temp. [K]　87.3

Molecular cross-sectional area [nm2]　0.1620

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

DH plot

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.).

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_{pn}. Total volume of pores which are still filled with adsorbate after the n-th step of desorption, $V\,[> r_{pn}]$, can be described as follows:

$$V\left[< \, r_{\mathrm{p}n}\right] = \int_{0}^{r_{\mathrm{p}n}} \pi\, r_{\mathrm{p}}{}^{2}\, L\left(r_{\mathrm{p}}\right) \mathrm{d}r_{\mathrm{p}} \tag{1}$$

Also the length and the surface area of pores which are emptied before the n-th step of desorption, $a\,[> r_{pn}]$ and $V\,[> r_{pn}]$ can be expressed as follows:

$$a\left[> \, r_{\mathrm{p}n}\right] = \int_{r_{\mathrm{p}n}}^{\infty} 2\,\pi\, r_{\mathrm{p}}\, L\left(r_{\mathrm{p}}\right) \mathrm{d}r_{\mathrm{p}} \tag{2}$$

$$L\left[> \, r_{\mathrm{p}n}\right] = \int_{r_{\mathrm{p}n}}^{\infty} L\left(r_{\mathrm{p}}\right) \mathrm{d}r_{\mathrm{p}} \tag{3}$$

where $L(r_p)$ expresses the length of pores which has radius of r_p. ΔV_n, the amount desorbed by the n-th step of desorption is:

$$\Delta V_{\mathrm{c}} = \Delta V_{n} - \Delta V_{\mathrm{m}} \tag{4}$$

where ΔV_c is the amount desorbed from capillary codensated state and ΔV_m is the amount desorbed from multilayer adsorbate. At this time, the volume of adsorbate in a pore of radius r_p (> r_{pn}) can be represented as follows:

$$\pi\left[r_{\mathrm{p}}{}^{2} - \left(r_{\mathrm{p}} - t_{n}\right)^{2}\right] L\left(r_{\mathrm{p}}\right) = \pi\left(2r_{\mathrm{p}}\, t_{n} - t_{n}{}^{2}\right) L\left(r_{\mathrm{p}}\right) \tag{5}$$

where t_n is the thickness of multilayer for the step n. The total multilayer adsorption in all pores or radii from r_{pn} to ∞ can be calculated by integration of (5) and the result can be rewritten by using (2) and (3) as follows.

$$\begin{aligned} V_{\mathrm{m}} &= \int_{r_{\mathrm{p}n}}^{\infty} \pi \left(2r_{\mathrm{p}}\, t_n - {t_n}^2\right) L(r_{\mathrm{p}})\, \mathrm{d}r_{\mathrm{p}} \\ &= t_n \int_{r_{\mathrm{p}n}}^{\infty} 2\,\pi\, r_{\mathrm{p}}\, L(r_{\mathrm{p}})\, \mathrm{d}r_{\mathrm{p}} - \pi\, {t_n}^2 \int_{r_{\mathrm{p}n}}^{\infty} L(r_{\mathrm{p}})\, \mathrm{d}r_{\mathrm{p}} \\ &= t_n\, a\left[> r_{\mathrm{p}n}\right] - \pi\, {t_n}^2\, L\left[> r_{\mathrm{p}n}\right] \end{aligned} \tag{6}$$

By differentiating (6) with respect to t_n, Equation (7) can be obtained and the volume change on n-th desorption step, ΔV_{m}, can be calculated from the eauation.

$$\mathrm{d}V_{\mathrm{m}} = \mathrm{d}t_n\, a\left[> r_{\mathrm{p}n}\right] - \pi\, 2\, t_n\, \mathrm{d}t_n\, L\left[> r_{\mathrm{p}n}\right] \tag{7}$$

Changing to Δ terms for finite steps:

$$\Delta V_{\mathrm{m}} = \Delta t_n\, a\left[> r_{\mathrm{p}n}\right] - \pi\, 2\, t_n\, \Delta t_n\, L\left[> r_{\mathrm{p}n}\right] \tag{8}$$

$a[> r_{pn}]$, $L[> r_{pn}]$ may be put in finite terms also, as the summations of length and area of pores involved in previous steps:

$$\Delta V_{\mathrm{m}} = \Delta t_n \sum a_{\mathrm{p}} - \pi\, 2\, t_n\, \Delta t_n \sum L_{\mathrm{p}} \tag{9}$$

From Equation (4) and (9), Equation (10) can be obtained.

$$\Delta V_{\mathrm{c}} = \Delta V_n - \Delta t_n \sum a_{\mathrm{p}} + \pi\, 2\, t_n\, \Delta t_n \sum L_{\mathrm{p}} \tag{10}$$

By using Equation (10), the change of pore volume ΔV_{p} can be calculated from ΔV_{C}.

$$\begin{aligned} \Delta V_{\mathrm{p}} &= \left(\frac{r_{\mathrm{p}}}{r_{\mathrm{k}} + \Delta t}\right)^2 \Delta V_{\mathrm{c}} \\ &= R_n \Delta V_{\mathrm{c}} \end{aligned} \tag{11}$$

where

$$R_n = \left(\frac{r_{\mathrm{p}}}{r_{\mathrm{k}} + \Delta t}\right)^2 \tag{12}$$

Thus Equation (10) can be rewritten as follows:

$$\Delta V_{\mathrm{p}} = R_n \left(\Delta V_n - \Delta t_n \sum a_{\mathrm{p}} + \pi\, 2\, t_n\, \Delta t_n \sum L_{\mathrm{p}}\right) \tag{13}$$

The increasing surface area of pores when desorption occures, a_{p} can be obtained by next equation.

$$a_{\mathrm{p}} = \frac{2\, \Delta V_{\mathrm{p}}}{r_{\mathrm{p}}} \tag{14}$$

And L_{p} , the length of the pores can be represented as follows:

$$L_{\mathrm{p}} = \frac{a_{\mathrm{p}}}{2\, \pi\, r_{\mathrm{p}}} \tag{15}$$

These two terms are summed line by line pore size distribution can be obtained by using Equation (13).

≪Reference≫

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

Operation

Operation of analysis software

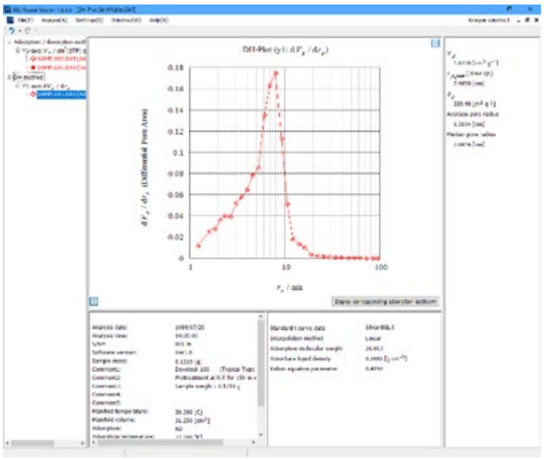
1 Select “Analysis(A)” and then “DH plot” from the analysis window menu.

- The software will execute a DH plot from adsorption or desorption branch of an adsorption isotherm.

→ Operation P.28 “Open file”

2 A DH-plot is displayed as shown right.

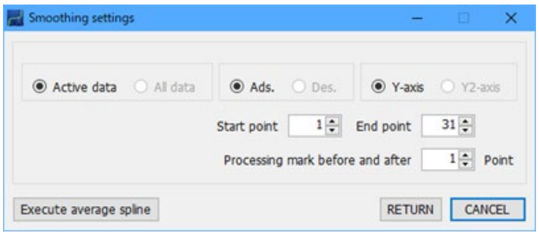
- The figure on the right is a DH-plot (differential pore area curve) of a nitrogen adsorption measurement on mesoporous silica.
- “silica-BEL.t” is used as a standard isotherm.



3 When you want to smooth the lines, select “Settings(S)” and then “Smoothing settings(S)” from the analysis window menu.

- The “Smoothing settings” window shown on the right will appear.

→ Operation P.43 “Smoothing settings”



● Active data ○ All data
● Ads. ○ Des.
● Y-axis ○ Y2-axis

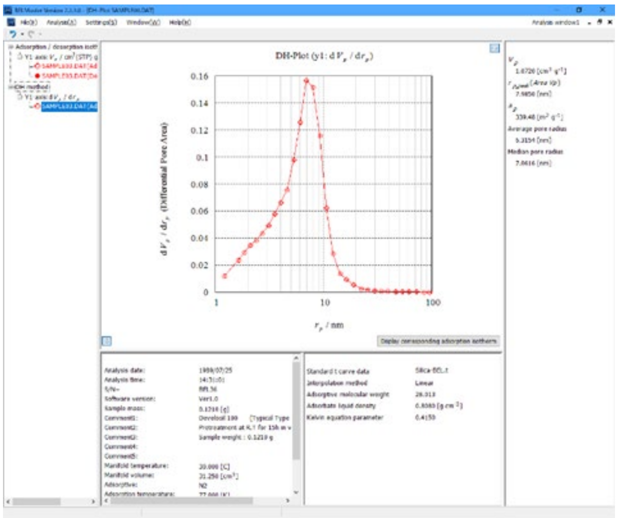
Start point 1
End point 31
Processing mark before and after 1 Point

About analysis result

The figure on the right shows the result of clicking the Execute average spline button to perform one round of smoothing.

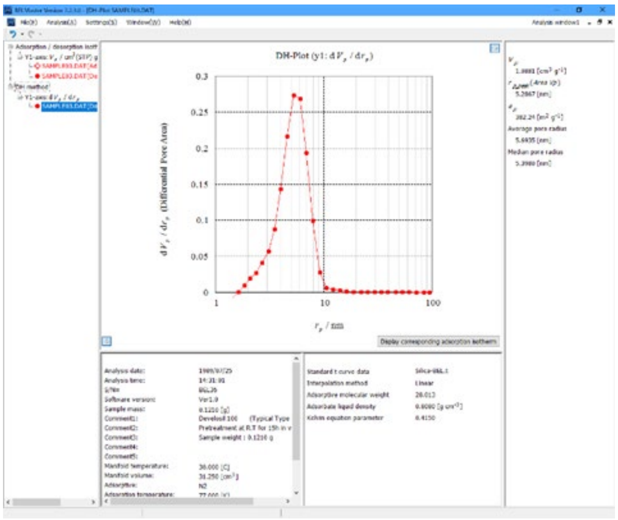
From the figure, it can be seen that this silica sample has mesopores of 2 to 15 nm radius, and has a distribution peak at 8.0 nm.

The integrated pore volume (V_p) will be 1.07 cm^3 g^{-1} and the integrated pore area (a_p) is 339 m^2 g^{-1}.

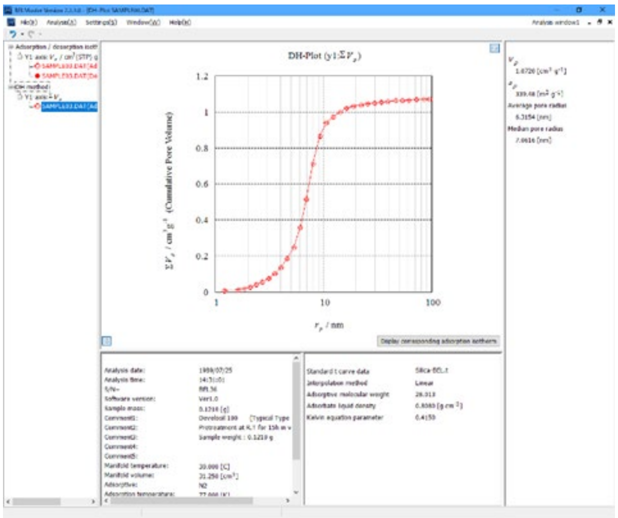


Select the desorption process for this silica sample in the "Analysis parameters" window.

The figure on the right shows the result of clicking the Execute average spline 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.



The figure on the right is a DH plot (integral curve) of the silica described before calculated from adsorption branch of its isotherm.



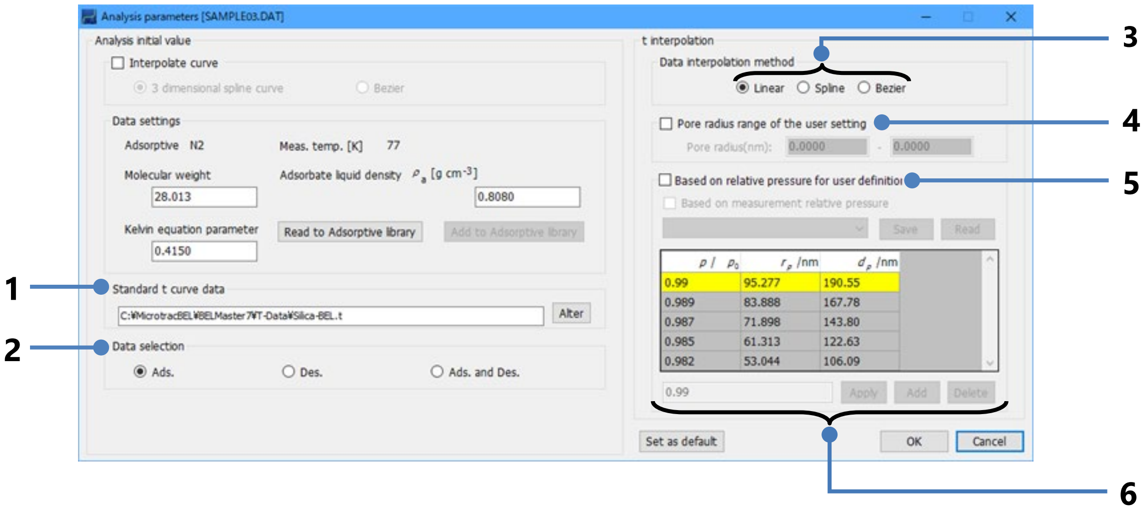
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Adsorptive N2

Meas. temp. [K] 77

Molecular weight 28.013

Adsorbate liquid density ρ_a [g cm^{-3}] 0.8080

Kelvin equation parameter 0.4150

Standard t curve data C:¥MicrotracBEL¥BELMaster7¥T-Data¥Silica-BEL.t

Data selection ● Ads. ○ Des. ○ Ads. and Des.

Data interpolation method ● Linear ○ Spline ○ Bezier

☐ Pore radius range of the user setting

Pore radius(nm): 0.0000 - 0.0000

☐ Based on relative pressure for user definitio

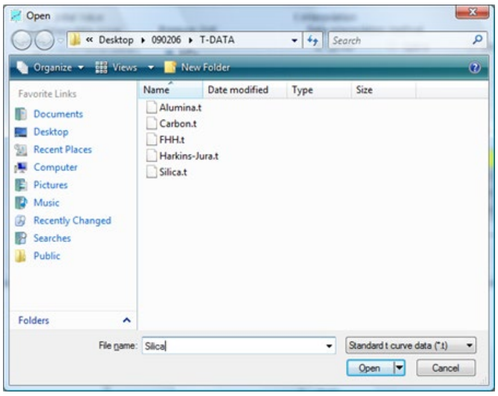
☐ Based on measurement relative pressure

p/p_0	r_p /nm	d_p /nm
0.99	95.277	190.55
0.989	83.888	167.78
0.987	71.898	143.80
0.985	61.313	122.63
0.982	53.044	106.09

0.99

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 right selection window will appear. Select a standard *t*-curve data file and click on the Open button.



Alumina.t
Carbon.t
FHH.t
Harkins-Jura.t
Silica.t

File name: Silica

Standard t curve data (*.t)

2 Select which data will be used for calculations, the adsorption branch or desorption branch.

- 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 branch, and the distribution of the bottle neck can be obtained from the desorption branch.
- When six pieces or more data are displayed, “Ads. and Des.” cannot be selected.

3 Select a method for interpolating the data file.

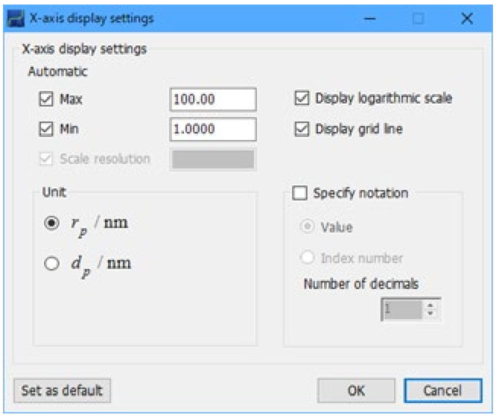
- In an adsorption / desorption isotherm, if you want to execute an interpolation using the same interpolation method, you can check whether the interpolation method is appropriate.

4	If [Pore diameter range of the user setting] is not selected, the software will calculate using the default range. ・When [Pore diameter range of the user setting] is selected, the software will calculate the pore diameter range specified in the table below. ・When the range is set, the ratio of whole pore volume to the pore volume in the range is calculated automatically.
5	If [Based on relative pressure for user definition] is selected, the software will calculate the plots with the relative pressure data below. ・When [Based on relative pressure for user definition] is not selected, the software will start calculating based on the default settings of relative pressure.
6	Relative pressure settings. ・When the [Based on relative pressure for 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. ・In the case the pressure measured in the data file is used, click on [Based on measurement relative pressure] and select the data in the pull down menu.

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

・r_p	the pore radius.
・d_p	the pore diameter.

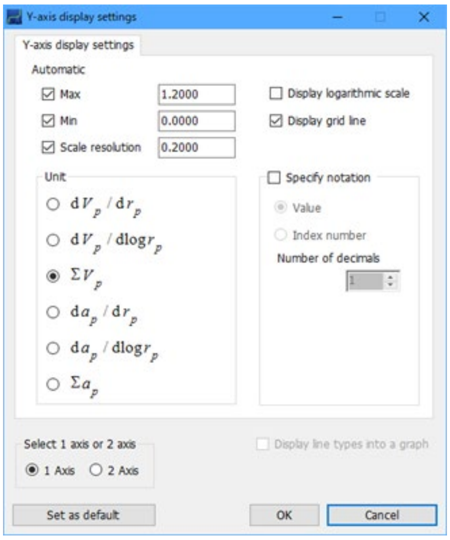


☑ Max 100.00
☑ Min 1.0000
☑ Scale resolution
☑ Display logarithmic scale
☑ Display grid line
● r_p / nm
○ d_p / nm
☐ Specify notation
● Value
○ Index number
Number of decimals 1

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

・ dV_p / dr_p	the area distribution.
・ $dV_p / d\log r_p$	the volume distribution.
・ ΣV_p	an Integral curve of volume.
・ da_p / dr_p	the length distribution.
・ $da_p / d\log r_p$	the area distribution.
・ Σa_p	an Integral curve of surface area.



Automatic
☑ Max 1.2000
☑ Min 0.0000
☑ Scale resolution 0.2000
☐ Display logarithmic scale
☑ Display grid line

Unit
○ dV_p / dr_p
○ $dV_p / d\log r_p$
● ΣV_p
○ da_p / dr_p
○ $da_p / d\log r_p$
○ Σa_p

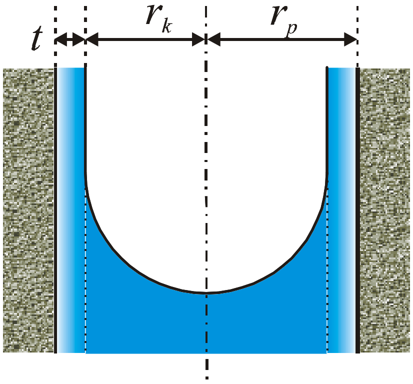
☐ Specify notation
● Value
○ Index number
Number of decimals 1

Select 1 axis or 2 axis
● 1 Axis ○ 2 Axis
☐ Display line types into a graph

BJH plot

Description

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 pore 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.

$$r_\mathrm{p} = t + r_\mathrm{k} \tag{1}$$

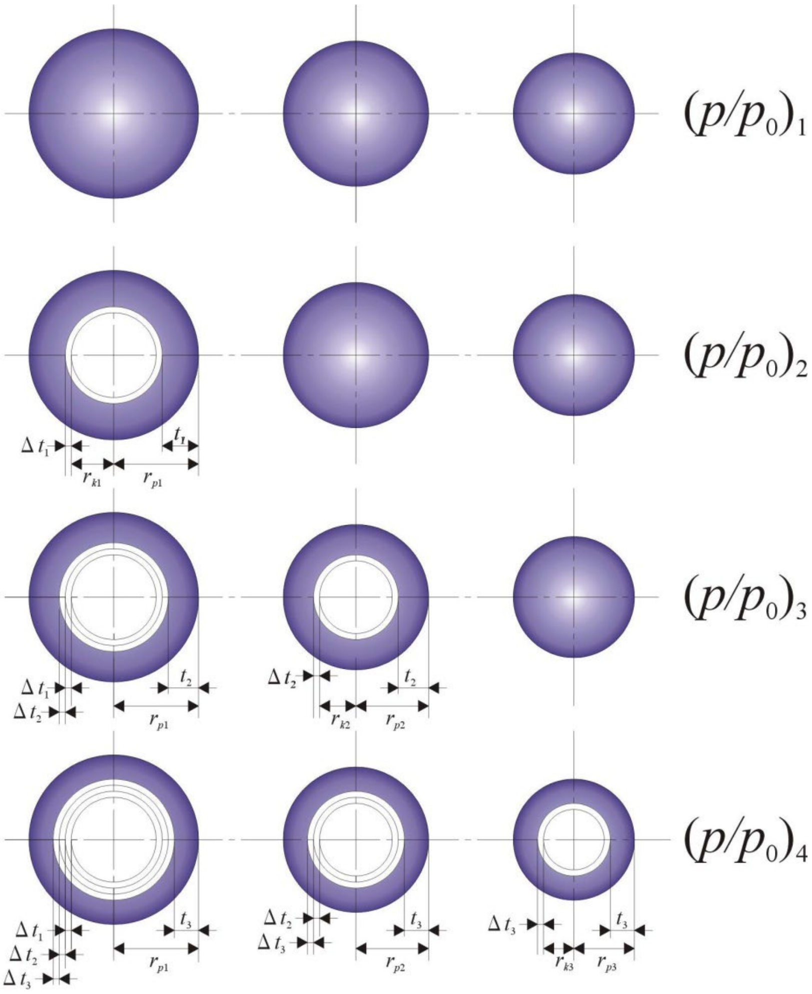
Thickness of adsorption layer can be calculated from t curve of standard sample, and core radius can be calculated by Kelvin Equation (2).

$$\ln\frac{p}{p_0} = -\frac{2\,\gamma\,V_\mathrm{L}}{R\,T}\frac{1}{r_\mathrm{m}} \tag{2}$$

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 (r_m) 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.

$$r_\mathrm{m} = \frac{0.953}{\ln\frac{p_0}{p}} \tag{3}$$

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 to 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 adsobate.

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 physisorbed layer Δt_1. V_{p1}, the volume of pores which has the largest pore radius r_{p1}, are expressed as follows:

$$\Delta V_1 \ = \ \pi \, (r_{\mathrm{k1}} + \ \Delta t_1)^2 \, L_1 \tag{4}$$

$$V_{\mathrm{p1}} \ = \pi \, {r_{\mathrm{p1}}}^2 \ L_1 \tag{5}$$

where L_1 is the total length of first pore (pore radius: r_{p1}). Thus, V_{p1} can be expressed as follows:

$$V_{\mathrm{p1}} \ = R_1 \, \Delta V_1 \tag{6}$$

where

$$R_1 = \frac{{r_{\mathrm{p1}}}^2}{(r_{\mathrm{k1}} + \ \Delta t_1)^2} \tag{7}$$

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 physisorbed layer left behind in the top layer. If the volume which is released by this thinning is designated as $V_{\Delta t2}$ then:

$$V_{p2} = R_2 \left(\Delta V_2 - \Delta V_{\Delta t_2}\right) \tag{8}$$

where

$$R_2 = \frac{{r_{p2}}^2}{(r_{k2} + \Delta t_2)^2} \tag{9}$$

Inspection of the figure above shows that

$$V_{\Delta t_2} = \pi L_1 (r_{k1} + \Delta t_1 + \Delta t_2)^2 - \pi L_1 (r_{k1} + \Delta t_1)^2 \tag{10}$$

Equation (10) 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:

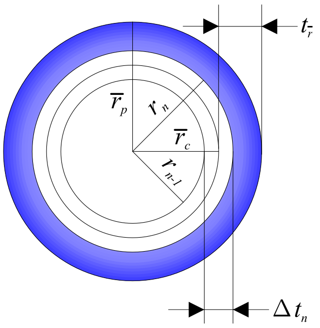
$$V_{\Delta t_2} = \Delta t_2 \times A_{c1} \tag{11}$$

where Ac_1 is average area from which the physisorbed gas is desorbed. Equation (11) can be generalized to express $V_{\Delta tn}$ when the pressure is lowered to $(p / p_0)_n$ as follows:

$$V_{\Delta t_n} = \Delta t_n \sum_{j=1}^{n-1} A_{cj} \tag{12}$$

Generalizing Equation (8) and substituting (12) for $V_{\Delta tn}$ yields:

$$V_{p\,n} = R_n \Delta V_n - R_n \Delta t_n \sum_{j=1}^{n-1} A_{cj} \tag{13}$$



(13) is complicated to carry out pore size distribution because A_c 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 right represents Δt_n, change in thickness of the physisorbed layer of a previously emptied pore of radius $\overline{r_p}$ during the n-th desorption step. In a desorption step, capillary radius changes from r_{n-1} to r_n. The average value of r_{n-1} and r_n is $\overline{r_c}$. Although A_c in Equation (13) varies actually before and after a desorption step, it can be represented using as $\overline{r_c}$ follows:

$$A_c = A_p \times \frac{\overline{r_c}}{\overline{r_p}} \tag{14}$$

Also $\overline{r_c}$ can be described as follows:

$$\overline{r_c} = \overline{r_p} - \overline{t_r} \tag{15}$$

where $\overline{t_{\rm r}}$ is the thickness of physisorbed layer at the corresponding value of $(p\,/\,p_0)$. Equation (13) can be rewritten as:

$$V_{{\rm p}\,n} = R_n\,\Delta V_n - R_n\,\Delta t_n \sum_{j=1}^{n-1} c_j\,A_{{\rm p}\,j} \tag{16}$$

where

$$c_j = \frac{\overline{r_{\rm p}} - \overline{t_{\rm r}}}{\overline{r_{\rm p}}} \tag{17}$$

$$R_n = \frac{{r_{{\rm p}\,n}}^2}{(r_{{\rm k}\,n-1} + \Delta t_n)^2} \tag{18}$$

$c_{\rm j}$ is a ratio of lateral area of two cylinders, one of which has a radius of $\overline{r_p}$ and another has a radius of $\overline{r_c}$. In other words, the amount desorbed is shown by the pore surface area assuming that the physisorbed layer of $\mathit{\Delta} t_n$ desorb from the wall of cylinder ($\overline{r_c}$). Even in the same pore, $c_{\rm j}$ value varies according to thickness of the physisorbed layer, i.e. c_j depends on the pressure. But in the original paper, they insisted that there was no big deal of error if c_j was treated as a constant c. Then they derived Equation (19) from Equation (16).

$$V_{{\rm p}\,n} = R_n\,\Delta V_n - R_n\,\Delta t_n\,c \sum_{j=1}^{n-1} A_{{\rm p}\,j} \tag{19}$$

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 (16) for pore size calculation without determining *c* value, which makes the calculation more accurate. Pore radius can be obtained from Equation (1), pore volume can be calculated from Equation (16) or (19). 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. Am. Chem. Soc.*, **73,** 373 (1951).

Operation

Operation of analysis software

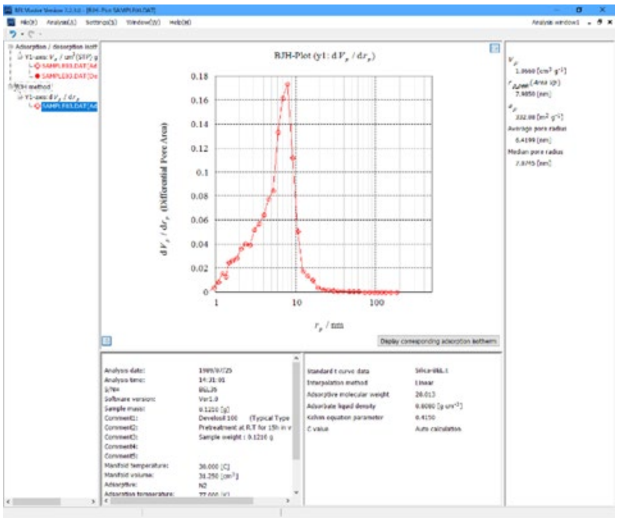
1 Select “Analysis(A)” and then “DH plot” from the analysis window menu.

- The software will execute a DH plot from adsorption or desorption branch of an adsorption isotherm.

→ Operation P.28 “Open file”

2 A BJH-plot is displayed as shown right.

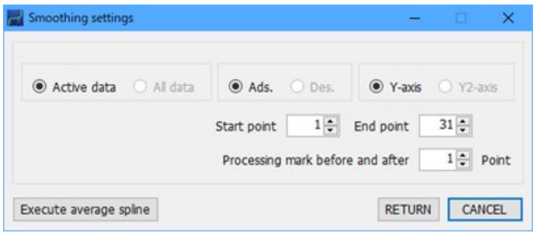
- The figure on the right is a BJH-plot (differential pore area curve) of a nitrogen adsorption isotherm for mesoporous silica.
- “silica-BEL.t” is used as a standard isotherm.



3 When you want to smooth the lines, select “Settings(S)” and then “Smoothing settings(S)” from the analysis window menu.

- The “Smoothing settings” window shown on the right will appear.

→ Operation P.43 “Smoothing settings”



● Active data ○ All data

● Ads. ○ Des.

● Y-axis ○ Y2-axis

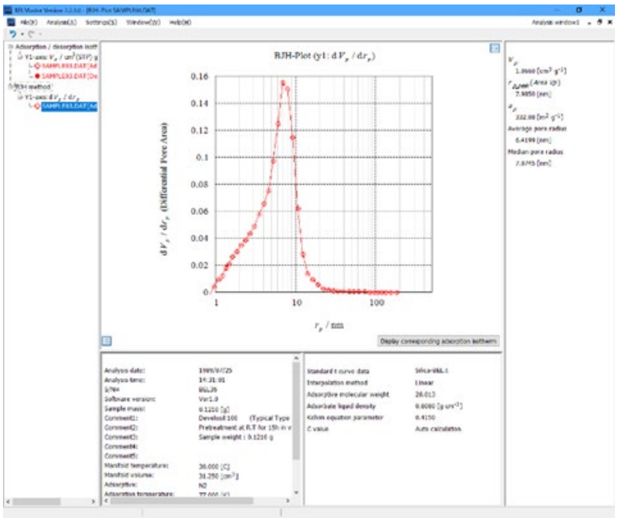
Start point 1　End point 31

Processing mark before and after 1 Point

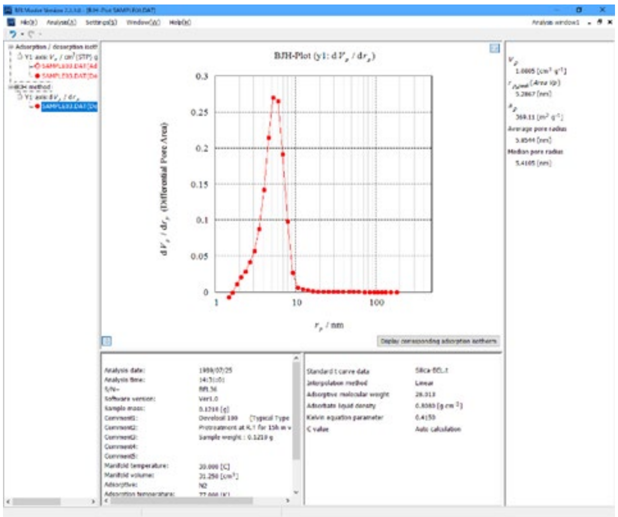
About analysis result

The figure on the right shows the result of clicking the Execute average spline button to perform one round of smoothing.

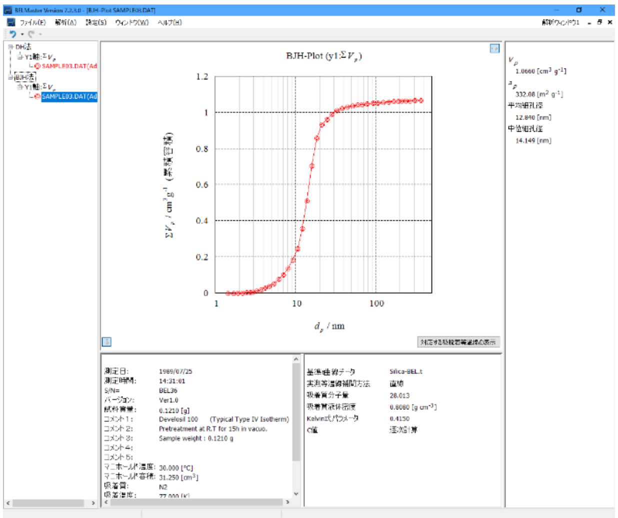
From the figure, it can be seen that this silica sample has mesopores of 2 to 15 nm radius, and it has a distribution peak at 8.0 nm. The integrated pore volume (V_p) will be 1.064 cm^3 g^{-1}.



Select the desorption process for this silica sample in the “Analysis parameters” window. The figure on the right shows the result of clicking the Execute average spline 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.



The figure on the right is a BJH plot (integral curve) of the silica described before calculated from adsorption branch of its isotherm.



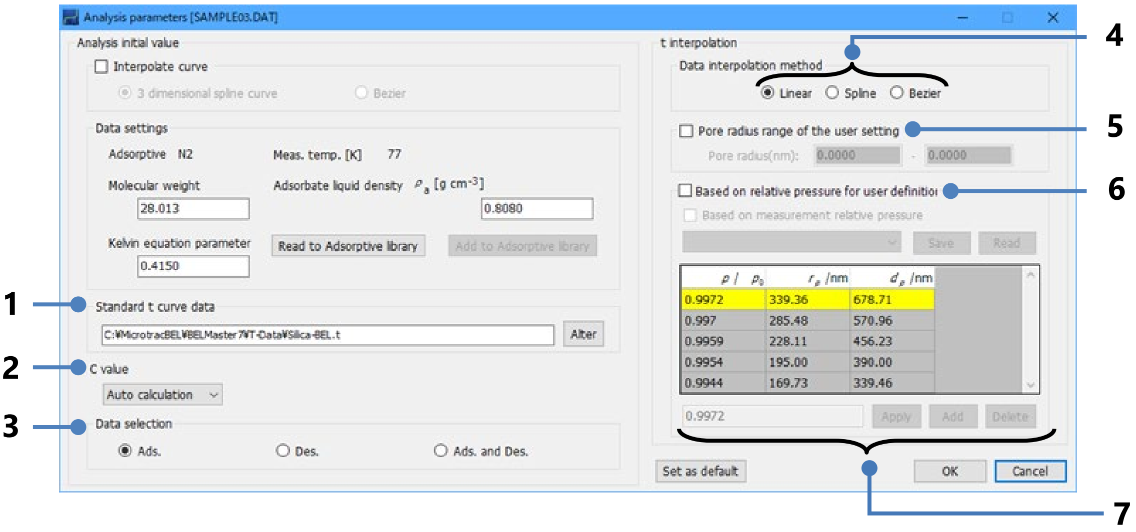
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



Analysis parameters [SAMPLE03.DAT]

Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve　○ Bezier

Data settings

Adsorptive　N2　　Meas. temp. [K]　77

Molecular weight　28.013

Adsorbate liquid density ρ_a [g cm^{-3}]　0.8080

Kelvin equation parameter　0.4150

Standard t curve data　C:¥MicrotracBEL¥BELMaster7¥T-Data¥Silica-BEL.t

C value　Auto calculation

Data selection　● Ads.　○ Des.　○ Ads. and Des.

t interpolation

Data interpolation method　● Linear　○ Spline　○ Bezier

☐ Pore radius range of the user setting

Pore radius(nm):　0.0000 - 0.0000

☐ Based on relative pressure for user definitio

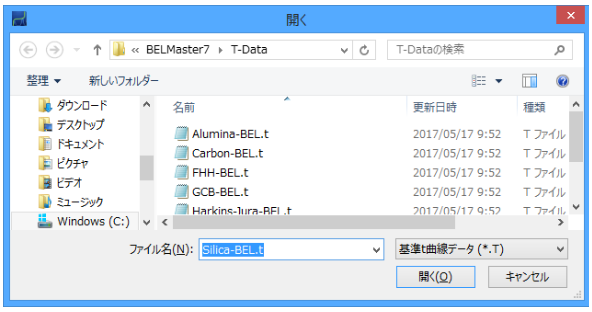
☐ Based on measurement relative pressure

p/p_0	r_p /nm	d_p /nm
0.9972	339.36	678.71
0.997	285.48	570.96
0.9959	228.11	456.23
0.9954	195.00	390.00
0.9944	169.73	339.46

0.9972

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 right selection window will appear. Select a standard *t*-curve data file and click on the Open button.



開く

BELMaster7 › T-Data

名前	更新日時	種類
Alumina-BEL.t	2017/05/17 9:52	T ファイル
Carbon-BEL.t	2017/05/17 9:52	T ファイル
FHH-BEL.t	2017/05/17 9:52	T ファイル
GCB-BEL.t	2017/05/17 9:52	T ファイル
Harkins-Jura-BEL.t	2017/05/17 9:52	T ファイル

ファイル名(N):　Silica-BEL.t

基準t曲線データ (*.T)

2　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.

3　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.
- When six pieces or more data are displayed, “Ads. and Des.” cannot be selected.

4　Select a method for interpolating the data file.

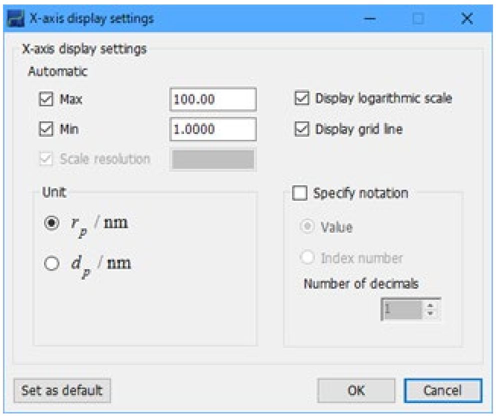
- If you want to execute an interpolation with the same interpolation method in an adsorption/desorption isotherm, you can check whether the interpolation method is appropriate.

5	If [Pore diameter range of the user setting] is not selected, the software will calculate using the default range. ・When [Pore diameter range of the user setting] is selected, the software will calculate the pore diameter range specified in the table below. ・When the range is set, the ratio of whole pore volume to the pore volume in the range is calculated automatically.
6	If [Based on relative pressure for user definition] is selected, the software will calculate the plots with the relative pressure data below. ・When [Based on relative pressure for user definition] is not selected, the software will start calculating based on the default settings of relative pressure.
7	Relative pressure settings ・When the [Based on relative pressure for 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. ・In the case the pressure measured in the data file is used, click on [Based on measurement relative pressure] and select the data in the pull down menu.

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

・r_p	the pore radius.
・d_p	the pore diameter.



X-axis display settings

X-axis display settings

Automatic

☑ Max 100.00

☑ Min 1.0000

☑ Scale resolution

☑ Display logarithmic scale

☑ Display grid line

Unit

● r_p / nm

○ d_p / nm

☐ Specify notation

● Value

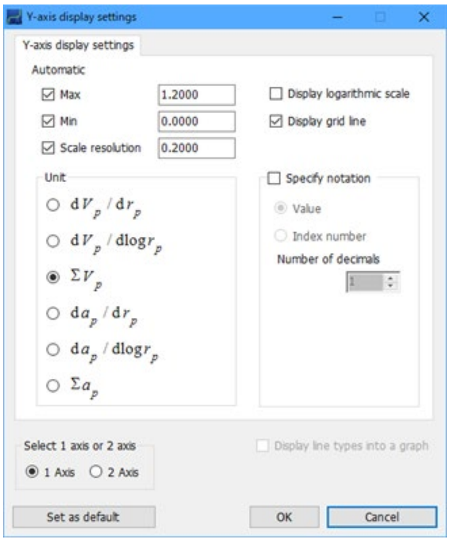
○ Index number

Number of decimals 1

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

・ dV_p / dr_p	the area distribution.
・ $dV_p / d\log r_p$	the volume distribution.
・ ΣV_p	an Integral curve of volume.
・ da_p / dr_p	the length distribution.
・ $da_p / d\log r_p$	the area distribution.
・ Σa_p	an Integral curve of surface area.



Y-axis display settings

Automatic

☑ Max 1.2000

☑ Min 0.0000

☑ Scale resolution 0.2000

☐ Display logarithmic scale

☑ Display grid line

Unit

○ dV_p / dr_p

○ $dV_p / d\log r_p$

● ΣV_p

○ da_p / dr_p

○ $da_p / d\log r_p$

○ Σa_p

☐ Specify notation

● Value

○ Index number

Number of decimals 1

Select 1 axis or 2 axis

● 1 Axis ○ 2 Axis

☐ Display line types into a graph

CI plot

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 or pore volume 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 $r + \delta r$, 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 $V_r\ \delta r$:

$$v_r\,\delta r = \frac{(r - t_r)^2}{r^2} V_r\,\delta r + \delta t \int_{r+\delta r}^{\infty} \frac{r - t_r}{r}\,\frac{2\,V_r}{r}\,\mathrm{d}r \tag{1}$$

The first term of the right-hand side represents the volume of nitrogen which has gone to fill pores by capillary condensation, 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 (1) can be rewritten as follows.

$$v_r\,\mathrm{d}r = \frac{(r - t_r)^2}{r^2} V_r\,\mathrm{d}r + \mathrm{d}t \int_{r+\delta r}^{\infty} \frac{2\,V_r\,(r - t_r)}{r^2}\,\mathrm{d}r \tag{2}$$

Consider a finite adsorption step from p_1 to p_2. With the increase 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:

$$v_{12} = \int_{r_1}^{r_2} v_r\,\mathrm{d}r = \int_{r_1}^{r_2} \frac{(r - t_1)^2}{r^2} V_r\,\mathrm{d}r + (t_2 - t_1)\int_{r_2}^{\infty} \frac{V_r\,(2r - t_1 - t_2)}{r^2}\,\mathrm{d}r \tag{3}$$

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. (3) can be converted into (4).

$$v_{12} = \frac{V_{12}}{r_2 - r_1}\int_{r_1}^{r_2} \frac{(r - t_1)^2}{r^2}\,\mathrm{d}r + (t_2 - t_1)\int_{r_2}^{\infty} \frac{V_r\,(2r - t_1 - t_2)}{r^2}\,\mathrm{d}r \tag{4}$$

where V_{12} is the volume of pores with radii between r_1 and r_2. To calculate pore volume, (4) is transformed as follows:

$$V_{12} = R_{12}\left(v_{12} - k_{12}\int_{r_2}^{\infty}\frac{r - t_{12}}{2\,r^2}\,V_{\mathrm{r}}\,\mathrm{d}r\right) \tag{5}$$

where

$$R_{12} = \frac{r_2 - r_1}{\int_{r_1}^{r_2}\frac{(r - t_1)^2}{r^2}\,\mathrm{d}r} \tag{6}$$

$$k_{12} = 4\,(t_2 - t_1) \tag{7}$$

$$t_{12} = \frac{t_1 + t_2}{2} \tag{8}$$

The integral term in Equation (5) is replaced by a summation term.

$$V_{12} = R_{12}\left(v_{12} - k_{12}\sum_{r_2+\frac{1}{2}\Delta r}^{r_{\mathrm{MAX}}}\frac{r - t_{12}}{2\,r^2}\,V_{\mathrm{r}}\,\Delta r\right) \tag{9}$$

Equation (19.10) can be derived by replacing pore radius in Equation (9) to pore diameter.

$$V_{12} = R_{12}\left(v_{12} - k_{12}\sum_{d_2+\frac{1}{2}\Delta d}^{d_{\mathrm{MAX}}}\frac{d - 2\,t_{12}}{d^2}\,V_{\mathrm{d}}\,\Delta d\right) \tag{10}$$

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≫

・ R. W. Cranston and F. A. Inkley, *Advan. Catalysis*, **9**, 143 (1957).

Operation

Operation of analysis software

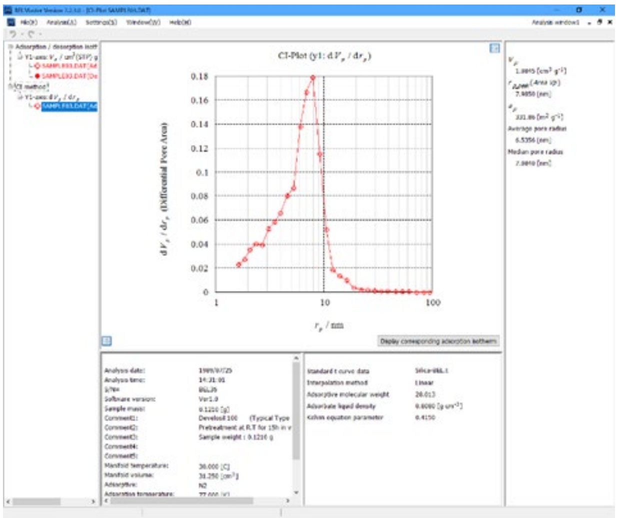
1 Select “Analysis(A)” and then “DH plot” from the analysis window menu.

- The software will execute a CI plot from adsorption or desorption branch of an adsorption isotherm.

→ Operation Operation P.28 “Open file”

2 A CI-plot is displayed as shown right.

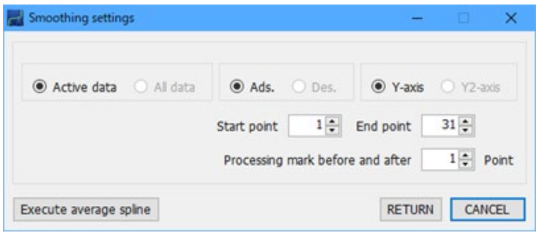
- The figure on the right is a CI-plot (differential pore area curve) of a nitrogen adsorption isotherm for mesoporous silica.
- “silica-BEL.t” is used as a standard isotherm.



3 When you want to smooth the lines, select “Settings(S)” and then “Smoothing settings(S)” from the analysis window menu.

- The “Smoothing settings” window shown on the right will appear.

→ Operation P.43 “Smoothing settings”



● Active data ○ All data

● Ads. ○ Des.

● Y-axis ○ Y2-axis

Start point 1

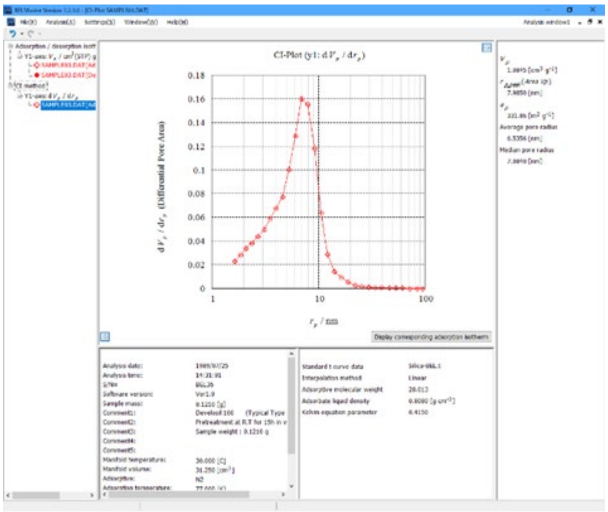
End point 31

Processing mark before and after 1 Point

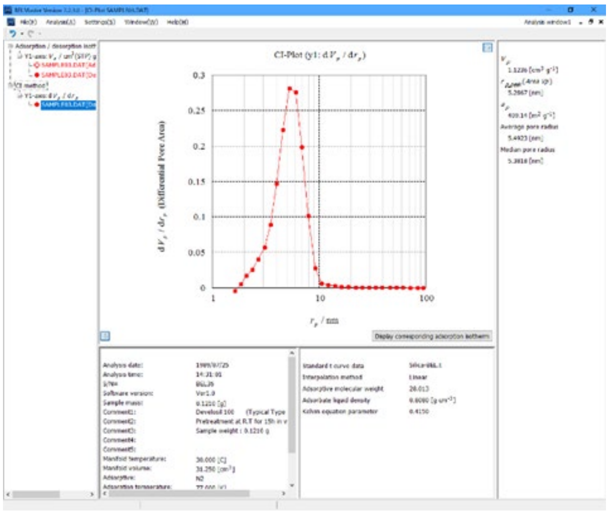
About analysis result

The figure on the right shows the result of clicking the Execute average spline button to perform one round of smoothing.

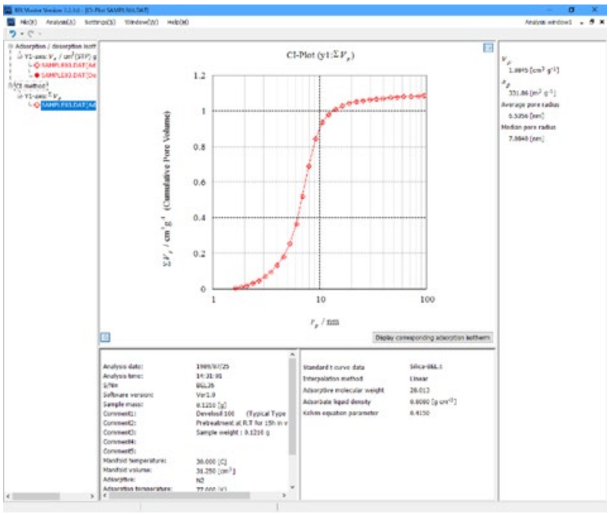
From the figure, it can be seen that this silica sample has mesopores of 2 to 15 nm radius, and has a distribution peak at 8.0 nm. The integrated pore volume (V_p) will be 1.085 cm^3 g^{-1} and the integrated pore area (a_p) is 332 m^2 g^{-1}.



Select the desorption branch to use for this silica sample on the "Analysis parameters" window. The figure on the right shows the result of clicking the Execute average spline 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.



The figure on the right is a CI-plot (integral curve) of the silica described before calculated from adsorption branch of its isotherm.



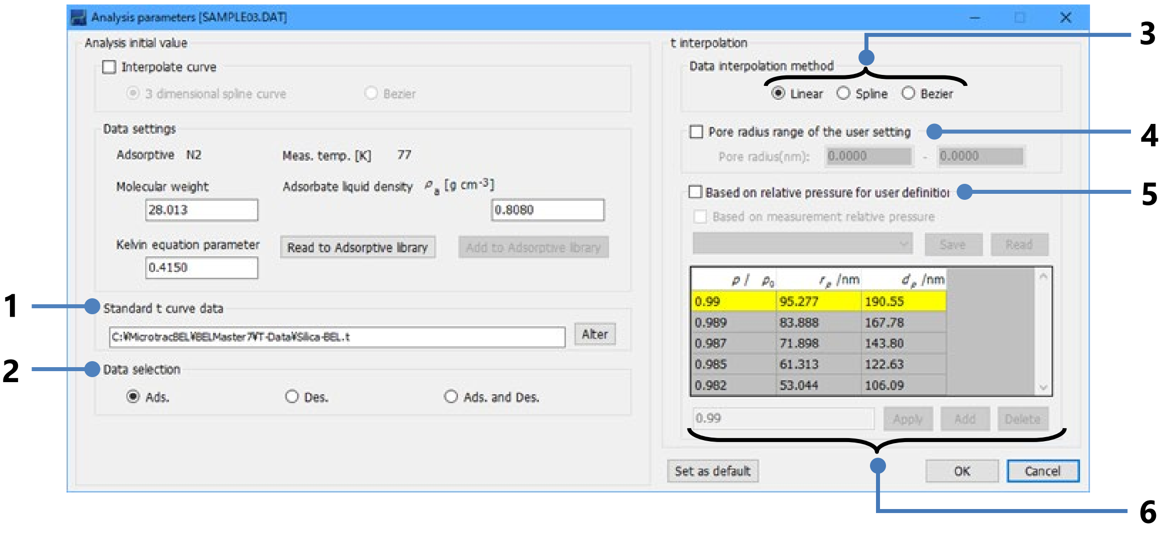
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



☐ Interpolate curve

Adsorptive N2

Meas. temp. [K] 77

Molecular weight 28.013

Adsorbate liquid density ρ_a [g cm^{-3}] 0.8080

Kelvin equation parameter 0.4150

Standard t curve data C:¥MicrotracBEL¥BELMaster7¥T-Data¥Silica-BEL.t

Data selection: ● Ads. ○ Des. ○ Ads. and Des.

Data interpolation method: ● Linear ○ Spline ○ Bezier

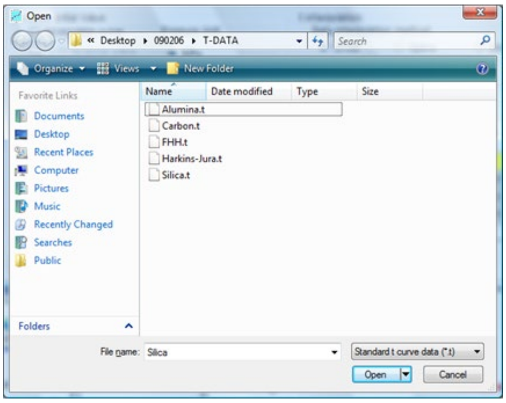
☐ Pore radius range of the user setting

Pore radius(nm): 0.0000 - 0.0000

☐ Based on relative pressure for user definitio

p / p_0	r_p /nm	d_p /nm
0.99	95.277	190.55
0.989	83.888	167.78
0.987	71.898	143.80
0.985	61.313	122.63
0.982	53.044	106.09

0.99

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 right selection window will appear. Select a standard *t*-curve data file and click on the Open button.	 Alumina.t Carbon.t FHH.t Harkins-Jura.t Silica.t File name: Silica Standard t curve data (*.t)
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. ・When six pieces or more data are displayed, adsorption/desorption cannot be selected.	
3	Select a method for interpolating the data file. ・In an adsorption/desorption 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 software will calculate using the default range.

- When [Pore diameter range of the user setting] is selected, the software will calculate the pore diameter range specified in the table below.
- When the range is set, the ratio of whole pore volume to the pore volume in the range is calculated automatically.

5 If [Based on relative pressure for user definition] is selected, the software will calculate the plots with the relative pressure data below.

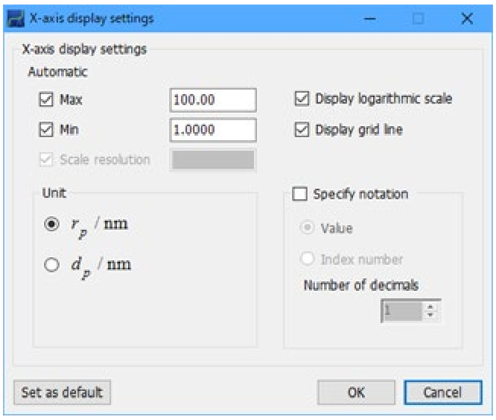
- When [Based on relative pressure for user definition] is not selected, the software will start calculating based on the default settings of relative pressure.

6 Relative pressure settings.

- When the [Pore diameter range of the user setting] 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.
- In the case the pressure measured in the data file is used, click on [Based on measurement relative pressure] and select the data in the pull down menu.

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.



X-axis display settings

X-axis display settings

Automatic

☑ Max 100.00

☑ Min 1.0000

☑ Scale resolution

☑ Display logarithmic scale

☑ Display grid line

Unit

● r_p / nm

○ d_p / nm

☐ Specify notation

● Value

○ Index number

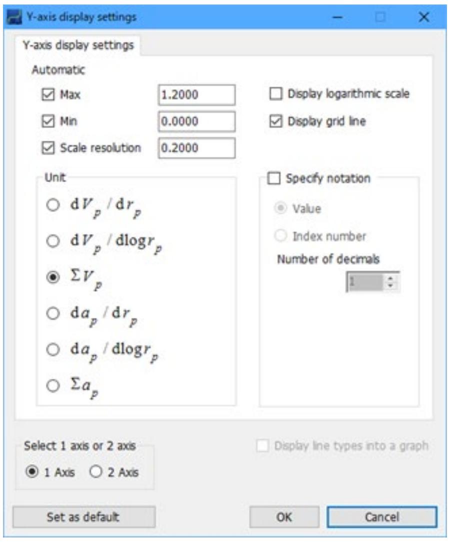
Number of decimals 1

- r_p the pore radius.
- d_p the pore diameter.

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

・ $dV_p\,/\,dr_p$	the area distribution.
・ $dV_p\,/\,d\log r_p$	the volume distribution.
・ ΣV_p	an Integral curve of volume.
・ $da_p\,/\,dr_p$	the length distribution.
・ $da_p\,/\,d\log r_p$	the area distribution.
・ Σa_p	an Integral curve of surface area.



Y-axis display settings

Automatic
☑ Max 1.2000
☑ Min 0.0000
☑ Scale resolution 0.2000
☐ Display logarithmic scale
☑ Display grid line

Unit
○ $dV_p\,/\,dr_p$
○ $dV_p\,/\,d\log r_p$
● ΣV_p
○ $da_p\,/\,dr_p$
○ $da_p\,/\,d\log r_p$
○ Σa_p

☐ Specify notation
● Value
○ Index number
Number of decimals 1

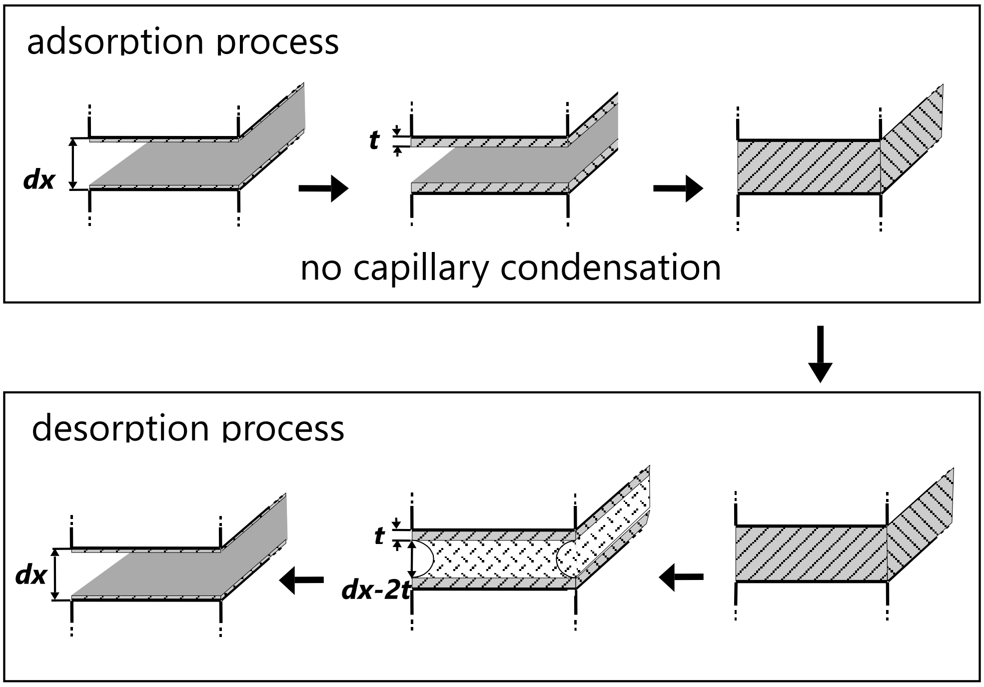
Select 1 axis or 2 axis
● 1 Axis ○ 2 Axis
☐ Display line types into a graph

INNES plot

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):

$$\ln\frac{p}{p_0} = -\frac{2\,\gamma\,V_\mathrm{L}}{R\,T}\,\frac{1}{dx-2t} \qquad (1)$$

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):

$$\ln \frac{p}{p_0} = -\frac{2\,\gamma\,V_{\mathrm{L}}}{R\,T}\,\frac{1}{r_{\mathrm{k}}} \tag{2}$$

In comparison between equations (1) and (2), we can see that r_k (Kelvin radius) for cylindrical mesopores corresponds to (*dx* - 2*t*) in the equation for slit-shaped mesopores.

Before calculation of mesopore distribution, substitute the following values into Equation (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 (1). Then, Equation (3) is obtained.

$$\mathrm{d}x - 2t = -\frac{0.415}{\log_{10}\dfrac{p}{p_0}}\ \mathrm{nm} \tag{3}$$

Regarding the slit-shaped mesopore as a parallel plate mode, the following equation is established.

$$X = V + A\,t \tag{4}$$

X = Amount (cm^3 g^{-1}) of nitrogen (adsorptive) adsorbed in liquid state
V = Volume (cm^3 g^{-1}) of nitrogen in liquid state when slit-shaped mesopore is fully filled
A = Surface area (m^2 g^{-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 ($\bar{A}$) of surface area (*A*) and an average value ($\bar{t}$) of adsorbate thickness (*t*).

$$\Delta X_i = \Delta V_i + \bar{A}_i\,\Delta t_i + \bar{t}_i\,\Delta A_i \tag{5}$$

ΔV can be expressed with the following equation, by using an average value (d_i) of the slit diameter.

$$\Delta V_i = \frac{-\,\bar{d}_i\,\Delta A_i}{2} \tag{6}$$

Substitute Equation (6) into Equation (5). Then, the following equation is established.

$$\Delta X_i = \Delta V_i + \bar{A}_i\,\Delta t_i - \frac{2\,\bar{t}_i}{\bar{d}_i}\Delta V_i \tag{7}$$

Transform Equation (7) to make Equation (8).

$$\Delta V_i = \frac{\bar{d}_i}{\bar{d}_i - 2\,\bar{t}_i}\left(\Delta X_i - \bar{A}_i\,\Delta t_i\right) \tag{8}$$

It is considered that the adsorbate is saturated in slit-shaped mesopores around high relative pressure. Therefore, equations V_0 = X_0 and *A* = 0, and the Equation (9) are established. Thus, Δ*V* can be obtained in each step:

$$\overline{A_{i+1}} = A_i + \Delta A_{i+1} \tag{9}$$

From the above equation, Δ*A* can be approximately expressed with the equation below.

$$\Delta A_i = \frac{\Delta X_i}{\Delta \bar{d}_i} \times \frac{\Delta V_{i-1}}{\Delta X_{i-1}} \tag{10}$$

Create a pore distribution curve by using "*dx*" obtained with Equation (3), and "Δ*V*" obtained with Equation (8).

≪Reference≫

・F. Rouquerol, J. Rouquerol & K. Sing "Adsorption by powders & porous solids (Academic Press, 1999)", 440.

・W. B. INNES, *Anal. Chem.*, **29**, 1069 (1957).

Operation

Operation of analysis software

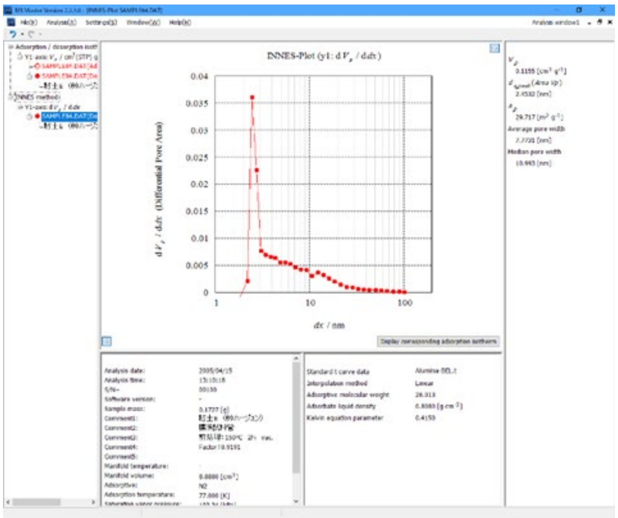
1 Select “Analysis(A)” and then “INNES plot” from the analysis window menu.

- The software will execute an INNES plot from desorption of an adsorption isotherm.

→ Operation P.28 “Open file”

2 A INNES-plot is displayed as shown right.

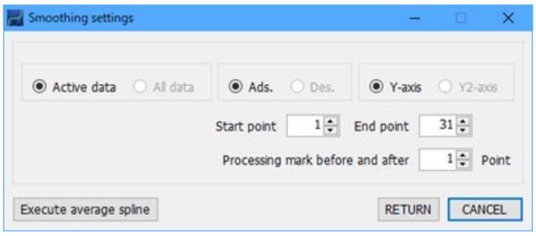
- The figure on the right shows an INNES-plot curve (differential pore area curve) obtained with measurement (desorption branch) of nitrogen adsorption into a clay mineral with slit-shaped pores.
- “Alumina-BEL.t” is specified as a standard isotherm.



3 When you want to smooth the lines, select “Settings(S)” and then “Smoothing settings(S)” from the analysis window menu.

- The “Smoothing settings” window shown on the right will appear.

→ Operation P.43 “Smoothing settings”



● Active data ○ All data

● Ads. ○ Des.

● Y-axis ○ Y2-axis

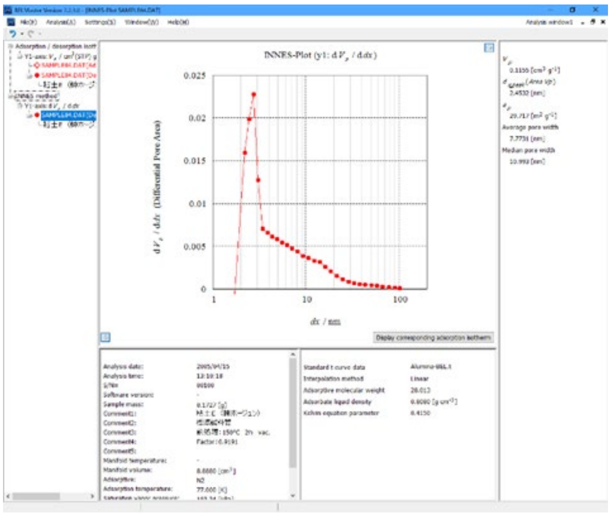
Start point 1

End point 31

Processing mark before and after 1 Point

About analysis result

Select the desorption branch for this clay mineral sample in the “INNES-plot setting” window. The figure on the right shows the result of clicking the Execute average spline button to perform one round of smoothing. From the figure, it can be seen that this silica sample has mesopores to 2 ~ 15 nm width, and has a distribution peak at 2.5 nm. The integrated pore volume (V_p) is 0.116 cm^3 g^{-1}, and the integrated pore area (S_p) is 29.9 m^2 g^{-1}.



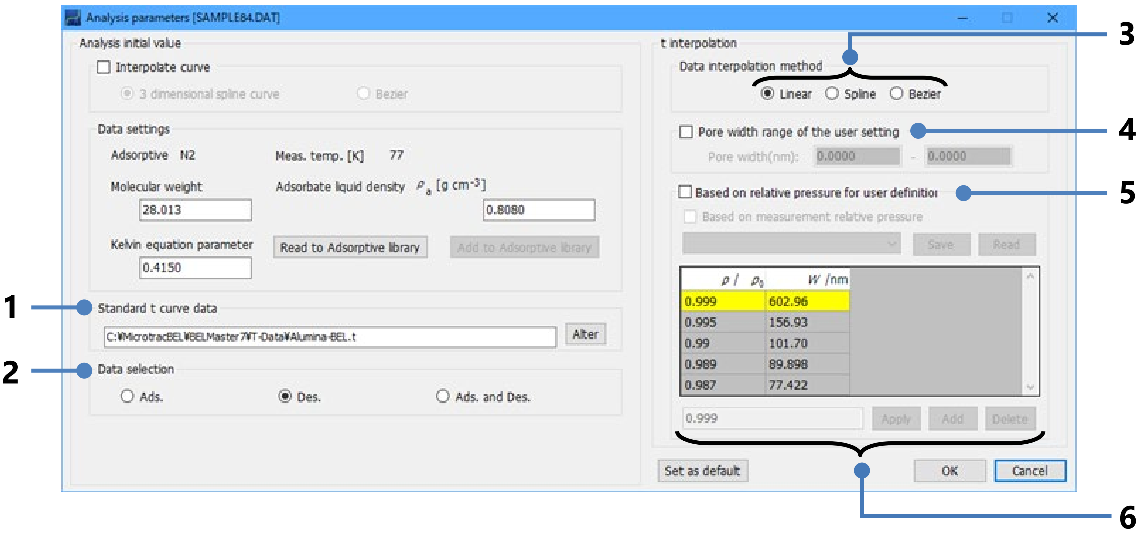
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



Analysis parameters [SAMPLE84.DAT]

Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Data settings

Adsorptive N2 Meas. temp. [K] 77

Molecular weight 28.013

Adsorbate liquid density ρ_a [g cm^{-3}] 0.8080

Kelvin equation parameter 0.4150

Standard t curve data C:¥MicrotracBEL¥BELMaster7¥T-Data¥Alumina-BEL.t

Data selection ○ Ads. ● Des. ○ Ads. and Des.

t interpolation

Data interpolation method ● Linear ○ Spline ○ Bezier

☐ Pore width range of the user setting

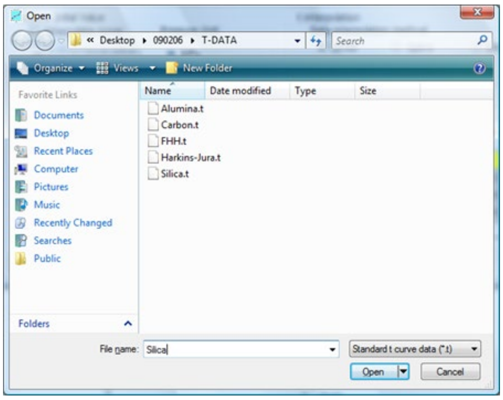
Pore width(nm): 0.0000 - 0.0000

☐ Based on relative pressure for user definitio

☐ Based on measurement relative pressure

p / p_0	W /nm
0.999	602.96
0.995	156.93
0.99	101.70
0.989	89.898
0.987	77.422

0.999

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 right selection window will appear. Select a standard *t*-curve data file and click on the Open button.	 Open « Desktop ▸ 090206 ▸ T-DATA Alumina.t Carbon.t FHH.t Harkins-Jura.t Silica.t File name: Silica Standard t curve data (*.t)
2	Select which data will be used for calculations, the adsorption side or desorption branch. ・To calculate pore distribution for slit-shaped mesopores, use desorption isotherm. For pore size 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. ・In an adsorption/desorption 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 software will calculate using the default range. ・When [Pore diameter range of the user setting] is selected, the software will calculate the pore diameter range specified in the table below. ・When the range is set, the ratio of whole pore volume to the pore volume in the range is calculated automatically.
5	If [Based on relative pressure for user definition] is selected, the software will calculate the plots with the relative pressure data below. ・When [Based on relative pressure for user definition] is not selected, the software will start calculating based on the default settings of relative pressure.
6	Relative pressure settings. ・When the [Pore diameter range of the user setting] 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. ・In the case the pressure measured in the data file is used, click on [Based on measurement relative pressure] and select the data in the pull down menu.

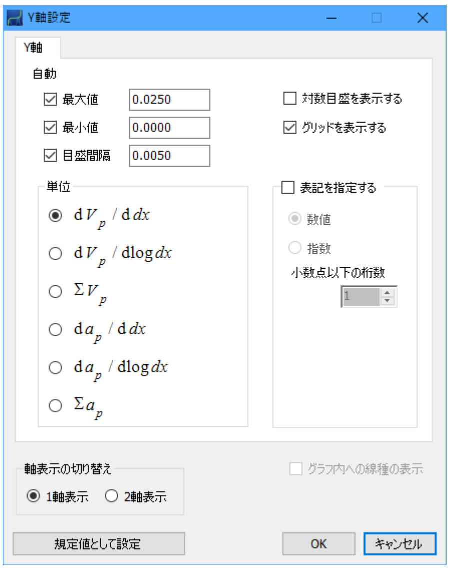
➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

・dV_p / ddx	the area distribution.
・dV_p / dlogdx	the volume distribution.
・ΣV_p	an Integral curve of volume.
・da_p / dr_p	the length distribution.
・da_p / dlogdx	the area distribution.
・Σa_p	an Integral curve of surface area.



☑ 最大値 0.0250
☑ 最小値 0.0000
☑ 目盛間隔 0.0050
☐ 対数目盛を表示する
☑ グリッドを表示する
● dV_p / ddx
○ dV_p / dlogdx
○ ΣV_p
○ da_p / ddx
○ da_p / dlogdx
○ Σa_p
☐ 表記を指定する
● 数値
○ 指数
小数点以下の桁数 1
軸表示の切り替え
● 1軸表示 ○ 2軸表示
☐ グラフ内への線種の表示

MP plot

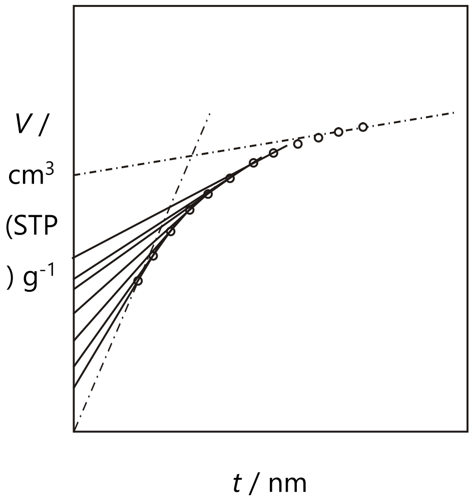
Description

In case of samples with micropores, the slope of t-plot decreases at a certain point (refer to "*t-plot*" (P.155)). If the size of micropores distribute uniformly, 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, actual 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 (s_2) of the straight line (L_2), which connects the 1st point and the 2nd point, is smaller than the slope (s_1) of the straight line (L_1), 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.

$$V_1 = (a_1 - a_2) \times \frac{(t_1 + t_2)}{2} \times 10^{-3} \qquad (1)$$

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 straight line that passes the original point, and a_2 is the one that is calculated from the other straight line. V_p is an integrated value of pore volume, which can be obtained in (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).

Operation

Operation of analysis software

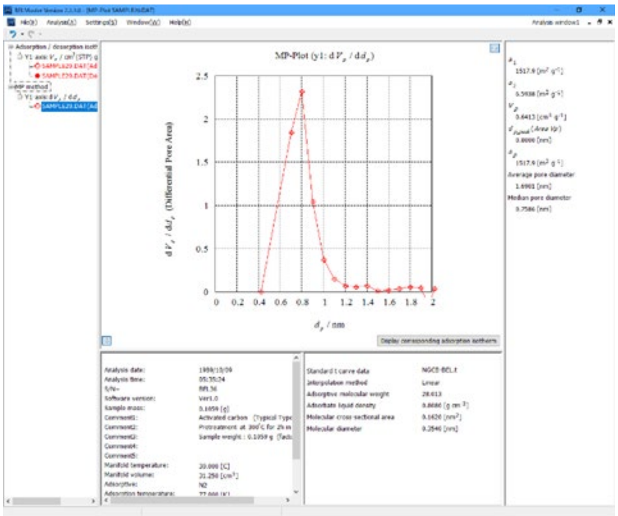
1 Select “Analysis(A)” and then “MP plot” from the analysis window menu.

- The software will execute an MP plot from adsorption branch of an adsorption isotherm.

→ Operation P.28 “Open file”

2 A MP-plot is displayed as shown right.

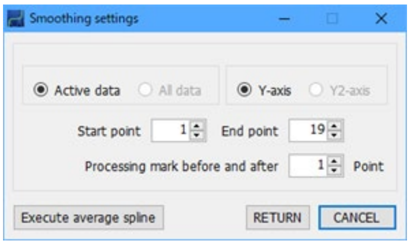
- The figure on the right is an MP-plot of a nitrogen adsorption measurement on microporous activated carbon.
- “NGCB-BEL.t” is used as a standard isotherm.



3 When you want to smooth the lines, select “Settings(S)” and then “Smoothing settings(S)” from the analysis window menu.

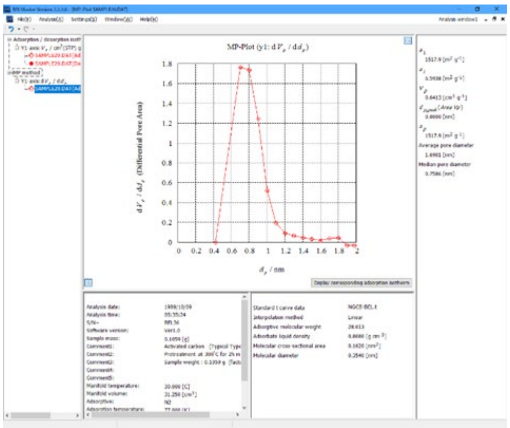
- The “Smoothing settings” window shown on the right will appear.

→ Operation P.43 “Smoothing settings”



● Active data ○ All data
● Y-axis ○ Y2-axis
Start point 1
End point 19
Processing mark before and after 1 Point

About analysis result



The figure on the right shows the result of clicking on the Execute average spline 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 software will calculate the total specific surface area (a_1 / m^2 g^{-1}). From the slope of the last straight line, the software 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 (P. 157).

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.

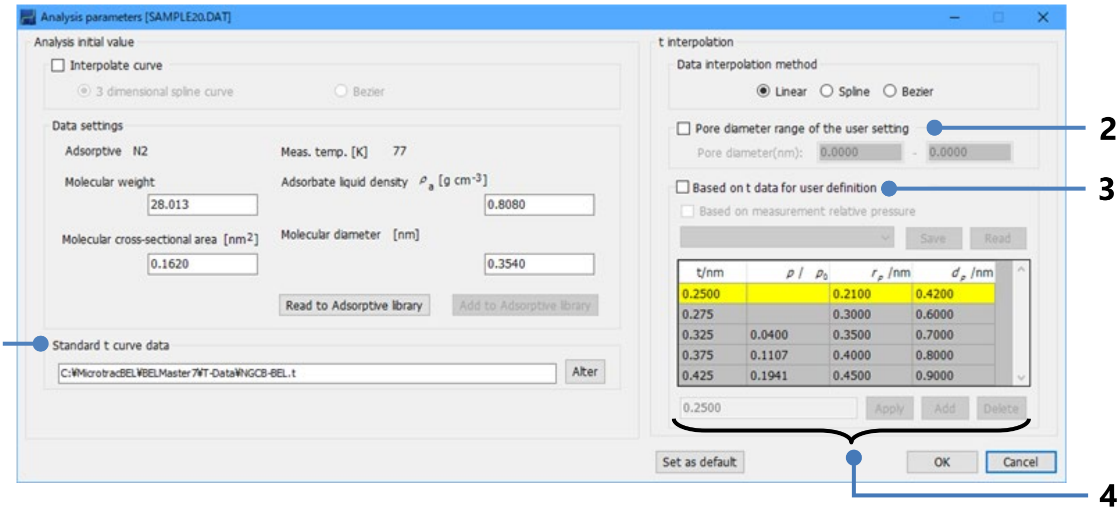
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



Analysis parameters [SAMPLE20.DAT]

Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Data settings

Adsorptive N2

Meas. temp. [K] 77

Molecular weight 28.013

Adsorbate liquid density ρ_a [g cm^{-3}] 0.8080

Molecular cross-sectional area [nm^2] 0.1620

Molecular diameter [nm] 0.3540

Standard t curve data

C:¥MicrotracBEL¥BELMaster7¥T-Data¥NGCB-BEL.t

t interpolation

Data interpolation method

● Linear ○ Spline ○ Bezier

☐ Pore diameter range of the user setting

Pore diameter(nm): 0.0000 - 0.0000

☐ Based on t data for user definition

☐ Based on measurement relative pressure

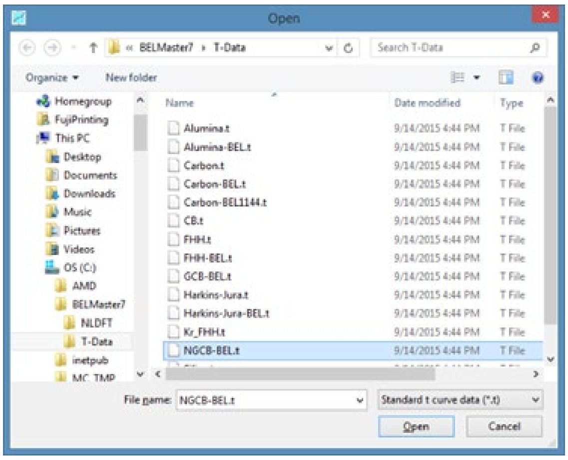
t/nm	p/p_0	r_p /nm	d_p /nm
0.2500		0.2100	0.4200
0.275		0.3000	0.6000
0.325	0.0400	0.3500	0.7000
0.375	0.1107	0.4000	0.8000
0.425	0.1941	0.4500	0.9000

0.2500

---

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 right selection window will appear. Select a standard *t*-curve data file and click on the Open button.



Name	Date modified	Type
Alumina.t	9/14/2015 4:44 PM	T File
Alumina-BEL.t	9/14/2015 4:44 PM	T File
Carbon.t	9/14/2015 4:44 PM	T File
Carbon-BEL.t	9/14/2015 4:44 PM	T File
Carbon-BEL1144.t	9/14/2015 4:44 PM	T File
CB.t	9/14/2015 4:44 PM	T File
FHH.t	9/14/2015 4:44 PM	T File
FHH-BEL.t	9/14/2015 4:44 PM	T File
GCB-BEL.t	9/14/2015 4:44 PM	T File
Harkins-Jura.t	9/14/2015 4:44 PM	T File
Harkins-Jura-BEL.t	9/14/2015 4:44 PM	T File
Kr_FHH.t	9/14/2015 4:44 PM	T File
NGCB-BEL.t	9/14/2015 4:44 PM	T File

File name: NGCB-BEL.t

Standard t curve data (*.t)

2 If [Pore diameter range of the user setting] is not selected, the software will calculate using the default range.

- When [Pore diameter range of the user setting] is selected, the software will calculate the pore diameter range specified in the table below.
- When the range is set, the ratio of whole pore volume to the pore volume in the range is calculated automatically.

3 If [Based on t data for user definition] is not selected, the software will calculate a *t*-plot using the default setting point.

- When [Based on t data for user definition] is selected, the software will calculate the *t* value specified in the table below.

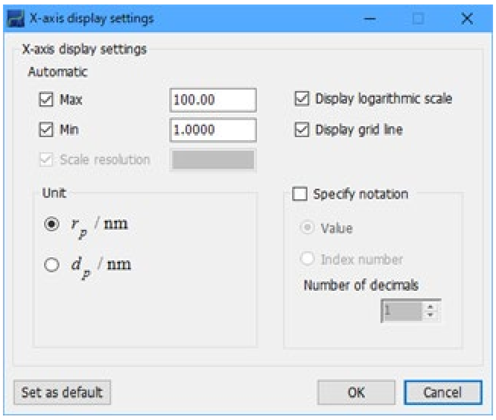
4 Relative pressure settings.

- When the [Based on t data for 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.
- In the case the pressure measured in the data file is used, click on [Based on measurement relative pressure] and select the data in the pull down menu.

➢ X axis display settings

Select "Settings(S)" → "X axis display settings(X)" to select desired unit of X axis.

・ r_p	the pore radius.
・ d_p	the pore diameter.



X-axis display settings

X-axis display settings

Automatic

☑ Max 100.00

☑ Min 1.0000

☑ Scale resolution

☑ Display logarithmic scale

☑ Display grid line

Unit

● r_p / nm

○ d_p / nm

☐ Specify notation

● Value

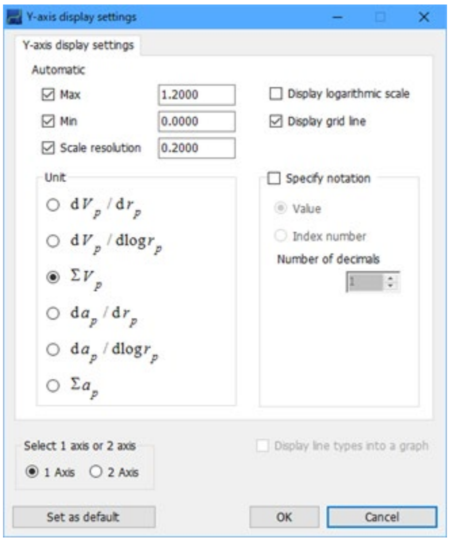
○ Index number

Number of decimals 1

➢ Y axis display settings

Select "Settings(S)" → "Y axis display settings(Y)" to select desired unit of Y axis.

・ dV_p / dr_p	the area distribution.
・ dV_p / dlog r_p	the volume distribution.
・ ΣV_p	an Integral curve of volume.
・ da_p / dr_p	the length distribution.
・ da_p / dlog r_p	the area distribution.
・ Σa_p	an Integral curve of surface area.



Y-axis display settings

Y-axis display settings

Automatic

☑ Max 1.2000

☑ Min 0.0000

☑ Scale resolution 0.2000

☐ Display logarithmic scale

☑ Display grid line

Unit

○ dV_p / dr_p

○ dV_p / dlogr_p

● ΣV_p

○ da_p / dr_p

○ da_p / dlogr_p

○ Σa_p

☐ Specify notation

● Value

○ Index number

Number of decimals 1

Select 1 axis or 2 axis

● 1 Axis ○ 2 Axis

☐ Display line types into a graph

HK plot

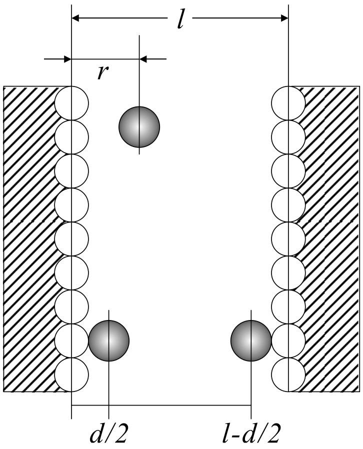
Description

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*.

$$U = C_m r^m - C_n r^n \tag{1}$$

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).



$$\phi = \frac{N_s A_s + N_a A_a}{2\,\sigma^4}\left[-\left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{l-r}\right)^4 + \left(\frac{\sigma}{l-r}\right)^{10}\right] \tag{2}$$

N_s indicates the number of atoms per adsorbent unit surface area, and N_a indicates the number of molecules per unit surface area of adsorbate (already adsorbed). A_s and A_a are constants determined by combination of adsorbent and adsorbate, which can be expressed by the following equation[2)].

$$A_s = \frac{6\,m\,c^2\,\alpha_s\,\alpha_a}{\dfrac{\alpha_s}{\chi_s} + \dfrac{\alpha_a}{\chi_a}} \tag{3}$$

$$A_a = \frac{3}{2}\,m\,c^2\,\alpha_s\,\alpha_a \tag{4}$$

m: Mass of electron, c: Speed of light
α_s, α_a : Polarizability of adsorbent atom and adsorbate molecule
χ_s, χ_a : Magnetic susceptibility of adsorbent atom and adsorbate molecule

σ is a distance that makes the interaction that adsorbate molecule receives zero. With the diameter of the adsorbent atom and adsorbate molecule, it can be expressed by the following equation.

$$\sigma = \left(\frac{2}{5}\right)^{\frac{1}{6}} \frac{d}{2} \tag{5}$$

$$d = d_{\mathrm{s}} + d_{\mathrm{a}} \tag{6}$$

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.

$$\bar{\phi} = \frac{N_{\mathrm{s}}\, A_{\mathrm{s}} + N_{\mathrm{a}}\, A_{\mathrm{a}}}{2\,\sigma^4\,(l - d)} \int_{\frac{d}{2}}^{l-\frac{d}{2}} \left[-\left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{l-r}\right)^4 + \left(\frac{\sigma}{l-r}\right)^{10} \right] \mathrm{d}r \tag{7}$$

On the other hand, considering thermodynamics, the energy required to adsorb 1 mol gas under pressure p is calculated from the following equation.

$$\epsilon = R\,T\,\ln(p_0\,/\,p) \tag{8}$$

L = Avogadro constant, from Equation (7) and (8),

$$R\,T\,\ln(p\,/\,p_0) = L\,\frac{N_{\mathrm{s}}\, A_{\mathrm{s}} + N_{\mathrm{a}}\, A_{\mathrm{a}}}{2\,\sigma^4\,(l - d)} \int_{\frac{d}{2}}^{l-\frac{d}{2}} \left[-\left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{l-r}\right)^4 + \left(\frac{\sigma}{l-r}\right)^{10} \right] \mathrm{d}r \tag{9}$$

After integration, the following equation, which shows the relation between l and p, can be derived.

$$R\,T\,\ln(p\,/\,p_0) = L\,\frac{N_{\mathrm{s}}\, A_{\mathrm{s}} + N_{\mathrm{a}}\, A_{\mathrm{a}}}{\sigma^4\,(l - d)} \left[\frac{\sigma^4}{3\left(l - \frac{d}{2}\right)^3} - \frac{\sigma^{10}}{9\left(l - \frac{d}{2}\right)^9} - \frac{\sigma^4}{3\left(\frac{d}{2}\right)^3} + \frac{\sigma^{10}}{3\left(\frac{d}{2}\right)^9} \right] \tag{10}$$

HK method was invented in order to calculate pore size distribution of activated carbon from nitrogen adsorption isotherm. Entering physicality values, it comes out as follows.

$$\ln(p\,/\,p_0) = \frac{62.38}{l - 0.64} \left[\frac{1.895\,\times 10^{-3}}{(l\,-\,0.32)^3} - \frac{2.7087\,\times 10^{-7}}{(l\,-\,0.32)^9} - 0.05014 \right] \tag{11}$$

In this 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.

≪Reference≫

1） G. Horváth, K. Kawazoe, *J. Chem. Eng. Japan*, **16**, 470 (1983).
2） J. G. Kirkwood, *Phys. Zeit.*, **33**, 57 (1932)
A. Muller, *Proc. Roy. Soc.*, **A154**, 624 (1936)

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)	1.02×10^{-24}	2.50×10^{-24}	1.46×10^{-24}	1.63×10^{-24}	2.91×10^{-24} 2)
Magnetic susceptibility χ (cm^3)	13.5×10^{-29}	1.30×10^{-29}	2.00×10^{-29}	3.25×10^{-29}	3.49×10^{-29} 2)
Density N (molecules m^{-2})	3.84×10^{19}	1.31×10^{19}	6.70×10^{18}	8.52×10^{18}	4.63×10^{18} 3)

1） K. Kutics, G. Horvath, Determination of Pore size distribution in MSC from Carbon-dioxide Adsorption 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

Operation of analysis software and analysis result

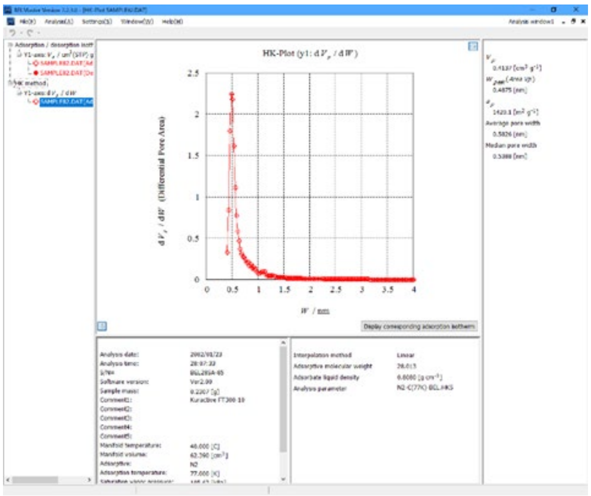
1 Select “Analysis(A)” and then “HK plot” from the analysis window menu.

- The software will execute a HK plot from adsorption branch of an adsorption isotherm.

→ Operation P.28 “Open file”

2 An HK-plot is displayed as shown right.

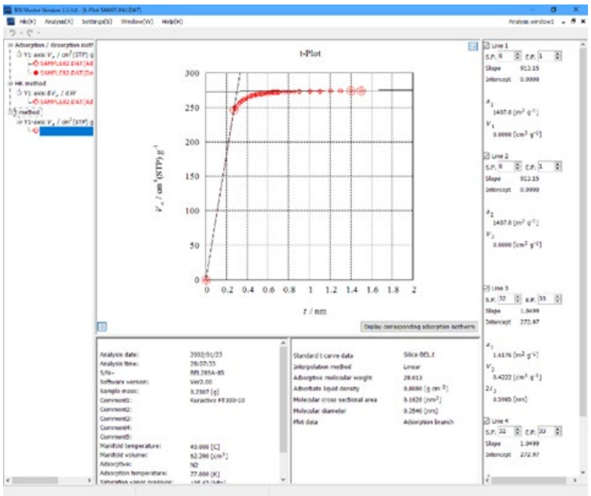
- The software will execute an HK plot using the specified conditions
- The figure on the right is an HK-plot measuring nitrogen adsorption by microporous activated carbon.



3 It can be seenthat this activated carbon has a large number of micropores 0.4 to 0.7 nm in width (*W*) and a distribution peak of 0.49 nm.

About analysis result

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.



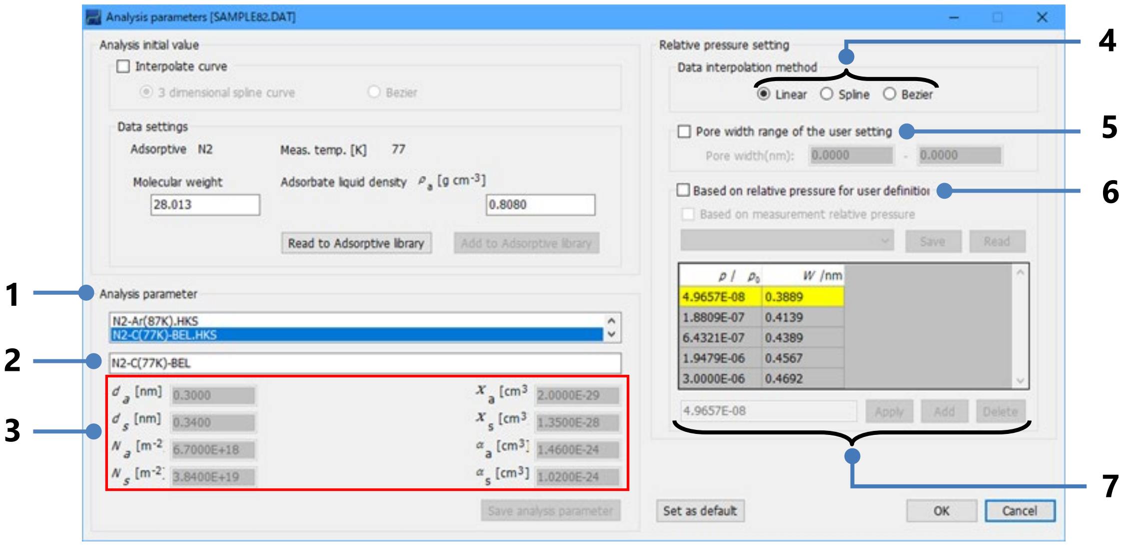
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37
- Parameters saved as “Ar-O (87K)-BEL.HKS”, “CO2-C (298K)-BEL.HKS”, “N2-C (77K)-BEL.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. (If “-BEL” is included, the file is not able to save.)



Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Data settings

Adsorptive N2

Meas. temp. [K] 77

Molecular weight 28.013

Adsorbate liquid density ρ_a [g cm^{-3}] 0.8080

Analysis parameter

N2-Ar(87K).HKS

N2-C(77K)-BEL.HKS

N2-C(77K)-BEL

d_a [nm] 0.3000

d_s [nm] 0.3400

N_a [m^{-2}] 6.7000E+18

N_s [m^{-2}] 3.8400E+19

χ_a [cm^3] 2.0000E-29

χ_s [cm^3] 1.3500E-28

α_a [cm^3] 1.4600E-24

α_s [cm^3] 1.0200E-24

Relative pressure setting

Data interpolation method

● Linear ○ Spline ○ Bezier

☐ Pore width range of the user setting

Pore width(nm): 0.0000 - 0.0000

☐ Based on relative pressure for user definitio

☐ Based on measurement relative pressure

p/p_0	W /nm
4.9657E-08	0.3889
1.8809E-07	0.4139
6.4321E-07	0.4389
1.9479E-06	0.4567
3.0000E-06	0.4692

4.9657E-08

1	Set a parameter. ・A parameter can be selected in this field, if any parameter has been registered.
2	A currently selected parameter is displayed. ・If you change the parameter in **3**, it should be changed to any item other than the default setting.
3	The parameter can be changed. ・The parameter name should be changed to any item other than the default setting in **2**. ・For the meaning of each parameter, refer to the following table.
4	Select a file data interpolation method. ・If you conduct curve interpolation of adsorption/desorption isotherm with the same interpolation method, it can be judged whether the interpolation method is proper or not.
5	Specify a calculation range with the pore width. ・If this checkbox is checked, the user-specified pore width is used for calculation. ・When the range is set, the ratio of whole pore volume to the pore volume in the range is calculated automatically.

6	Relative pressure data of user definition is used as standard. ・If this checkbox is unchecked, the default point is used for calculation. If this checkbox is checked, the following table can be edited.
7	Edit the relative pressure set value. ・When the [Based on relative pressure of user definition] checkbox is checked, this table can be edited. ・When the checkbox for [Based on measurement relative pressure] is checked, pore width is calculated with relative pressure at a measurement point on the adsorption/desorption isotherm. ・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.

Parameter	Mean	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	atoms 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

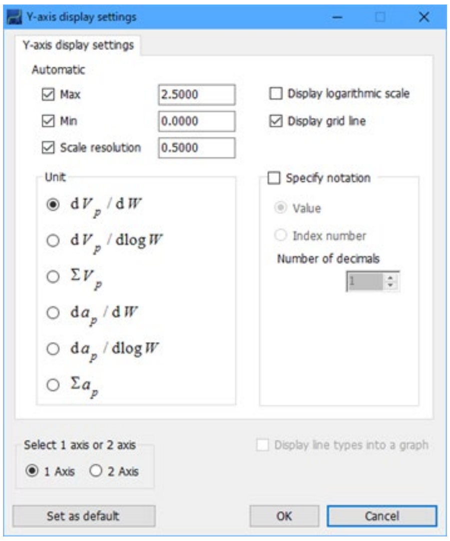
➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

・ dV_p / dW	the area distribution.
・ $dV_p / d\log W$	the volume distribution.
・ ΣV_p	an Integral curve of volume.
・ da_p / dW	the length distribution.
・ $da_p / d\log W$	the area distribution.
・ Σa_p	an Integral curve of surface area.



Y-axis display settings

Y-axis display settings

Automatic

☑ Max 2.5000

☑ Min 0.0000

☑ Scale resolution 0.5000

☐ Display logarithmic scale

☑ Display grid line

Unit

● dV_p / dW

○ $dV_p / d\log W$

○ ΣV_p

○ da_p / dW

○ $da_p / d\log W$

○ Σa_p

☐ Specify notation

● Value

○ Index number

Number of decimals 1

Select 1 axis or 2 axis

● 1 Axis ○ 2 Axis

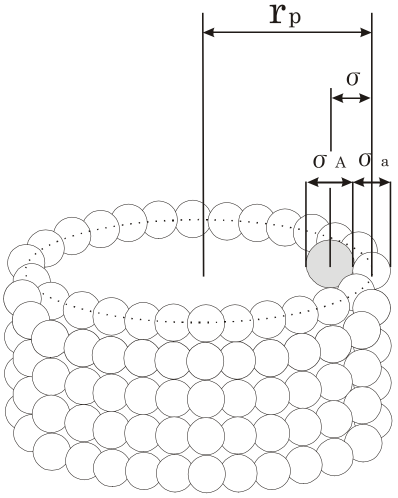
☐ Display line types into a graph

SF plot

Description

As mentioned in “HK plot”, for carbonaceous slit-shaped microporous materials such as active carbon, Horvath and Kawazoe made it possible to calculate micropore distribution by deriving the Equation (11) of “HK plot” from Hill’s view1) of the average potential of N_2 molecules in micorpore.
Saito and Foley applied this idea of average potential to cylinder-shaped micropore using Everett and Powl’s view of potential2), and succeeded to calculate micropore distribution of zeolite, $AlPO_4$ and etc3)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. This 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 Equation (10) of “HK plot”.

$$\ln(p\,/\,p_0) = \frac{3\,\pi\,L}{4\,R\,T}\frac{N_s\,A_s + N_a\,A_a}{\sigma^4}\sum_{k=0}^{\infty}\left[\frac{1}{k+1}\left(1-\frac{\sigma}{r_p}\right)^{2k}\left\{\frac{21}{32}\,\alpha_k\left(\frac{\sigma}{r_p}\right)^{10} - \beta_k\left(\frac{\sigma}{r_p}\right)^{4}\right\}\right] \tag{1}$$

α_k and β_k are indicated Γ function and calculated from the following formulas.

$$\alpha_k{}^{0.5} = \frac{\Gamma(-4.5)}{\Gamma(-4.5-k)\,\Gamma(k+1)} \tag{2}$$

$$\beta_k{}^{0.5} = \frac{\Gamma(-1.5)}{\Gamma(-1.5-k)\,\Gamma(k+1)} \tag{3}$$

Please refer to HK method analysis (HK plot) 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 Equation (1) are as indicated in the table below. The following equation is derived from the calculation of each parameter of (24.1) based on Table 1.

Table2 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 m^{-2})	1.31×10^{19}	8.52×10^{18}

4) A. Saito, H. C. Foley, *Microporous Materials*, **3** (1995) 531

$$\ln(p / p_0) = \varepsilon^* \sum_{k=0}^{\infty} \left[\frac{1}{k+1} \left(1 - \frac{0.306}{r_\mathrm{p}}\right)^{2k} \left\{ \frac{21}{32} \alpha_k \left(\frac{0.306}{r_\mathrm{p}}\right)^{10} - \beta_k \left(\frac{0.306}{r_\mathrm{p}}\right)^{4} \right\} \right] \tag{4}$$

where

$$\alpha_k = \left(\frac{-4.5-k}{k}\right)^2 \alpha_{k-1} \tag{5}$$

$$\beta_k = \left(\frac{-1.5-k}{k}\right)^2 \beta_{k-1} \tag{6}$$

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 (4). Integral curve can be obtained by calculating the adsorption amount against relative pressure that is obtained from (4) 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, 668(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 Mater.*, **3**, 531 (1995)

Operation

Operation of analysis software and analysis result

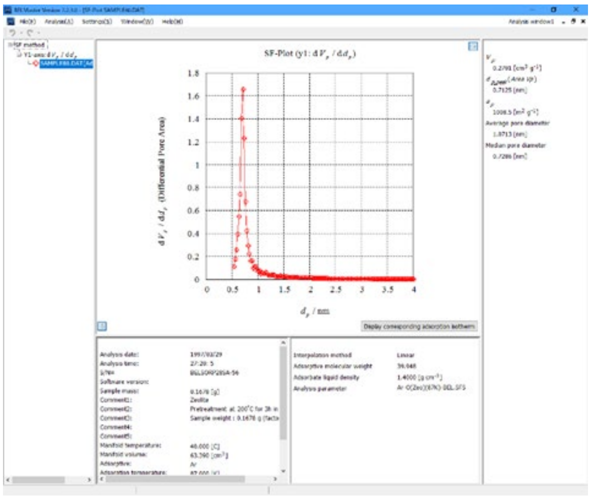
1 Select “Analysis(A)” and then “SF plot” from the analysis window menu.

- The software will execute an SF plot from adsorption branch of an isotherm.

→ Operation P.28 “Open file”

2 An SF-plot is displayed as shown right.

- The software will execute an SF-plot using the specified conditions.
- The figure on the right is an SF-plot of an argon isotherm for microporous zeolite.



3 It can be seen that this zeolite has a large number of micropores 0.5 to 0.9 nm in diameter (d_p), and a distribution peak at 0.74 nm.

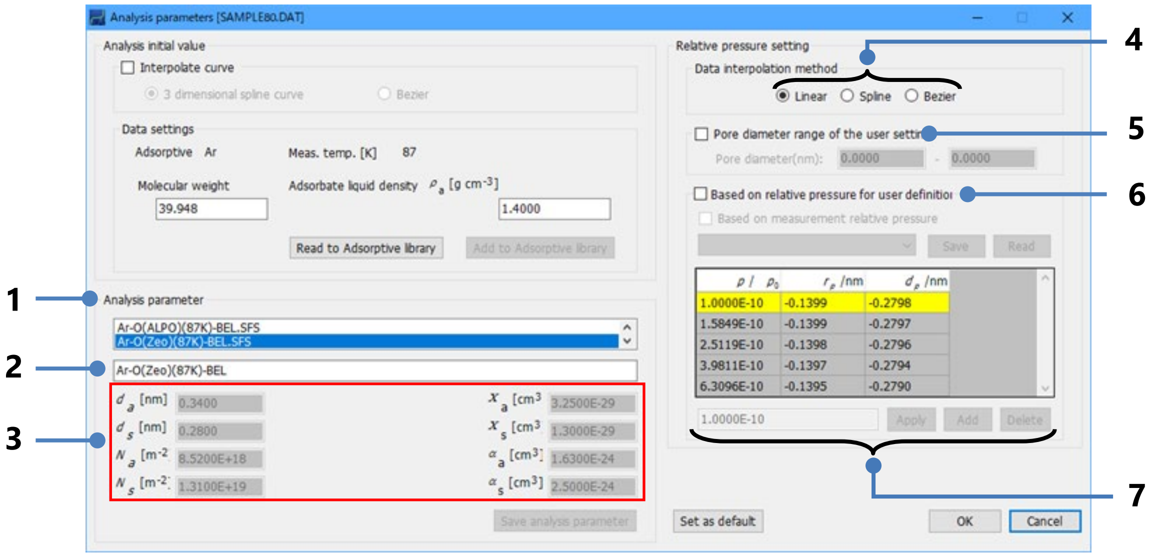
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37
- 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(ALPO)(87K)-BEL.SFS” and “Ar-O(Zeo)(87K)-BEL.SFS” cannot be changed. Change the name of the file being displayed and then you can change the settings. Click on the OK button. (If “-BEL” is included, the file is not able to save.)



Adsorptive Ar

Meas. temp. [K] 87

Molecular weight 39.948

Adsorbate liquid density ρ_a [g cm^{-3}] 1.4000

Ar-O(ALPO)(87K)-BEL.SFS
Ar-O(Zeo)(87K)-BEL.SFS

Ar-O(Zeo)(87K)-BEL

d_a [nm] 0.3400
d_s [nm] 0.2800
N_a [m^{-2}] 8.5200E+18
N_s [m^{-2}] 1.3100E+19
χ_a [cm^3] 3.2500E-29
χ_s [cm^3] 1.3000E-29
α_a [cm^3] 1.6300E-24
α_s [cm^3] 2.5000E-24

Pore diameter(nm): 0.0000 - 0.0000

p/p_0	r_p /nm	d_p /nm
1.0000E-10	-0.1399	-0.2798
1.5849E-10	-0.1399	-0.2797
2.5119E-10	-0.1398	-0.2796
3.9811E-10	-0.1397	-0.2794
6.3096E-10	-0.1395	-0.2790

1.0000E-10

1	Set a parameter. ・A parameter can be selected in this field, if any parameter has been registered.
2	A currently selected parameter is displayed. ・If you change the parameter in **3**, it should be changed to any item other than the default setting.
3	The parameter can be changed. ・The parameter name should be changed to any item other than the default setting in **2**. ・For the meaning of each parameter, refer to the following table.
4	Select a file data interpolation method. ・If you conduct curve interpolation of adsorption/desorption isotherm with the same interpolation method, it can be judged whether the interpolation method is proper or not.
5	Specify a calculation range with the pore width. ・If this checkbox is checked, the user-specified pore width is used for calculation. ・When the range is set, the ratio of whole pore volume to the pore volume in the range is calculated automatically.

5	Relative pressure data of user definition is used as standard. ・If this checkbox is unchecked, the default point is used for calculation. If this checkbox is checked, the following table can be edited.
6	Edit the relative pressure set value. ・When the [Based on relative pressure of user definition] checkbox is checked, this table can be edited. ・When the checkbox for [Based on measurement relative pressure] is checked, pore diameter is calculated with relative pressure at a measurement point on the adsorption/desorption isotherm. ・Pressing the Alter button changes data in the selected cell (indicated in yellow) to a 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.

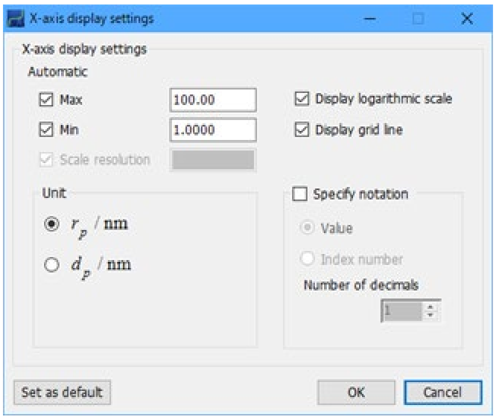
Parameter	Adsorbate molecular diameter	Unit
d_a	Adsorbate molecular diameter	nm
d_s	Adsorbent atom diameter	nm
N_a	Number of adsorbate molecules adsorbed per unit surface area	molecules m^{-2}
N_s	Number of adsorbent atoms per unit surface area	atoms m^{-2}
X_a	Magnetic susceptibility of the adsorbate 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

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

・r_p the pore radius.

・d_p the pore diameter.



X-axis display settings

☑ Max 100.00

☑ Min 1.0000

☑ Scale resolution

☑ Display logarithmic scale

☑ Display grid line

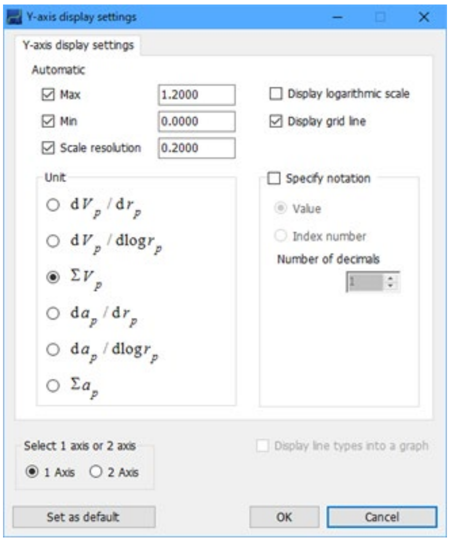
Unit: ● r_p / nm ○ d_p / nm

☐ Specify notation: ● Value ○ Index number

Number of decimals 1

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.



Y-axis display settings

Automatic

☑ Max 1.2000

☑ Min 0.0000

☑ Scale resolution 0.2000

☐ Display logarithmic scale

☑ Display grid line

Unit

○ dV_p / dr_p

○ dV_p / $d\log r_p$

● ΣV_p

○ da_p / dr_p

○ da_p / $d\log r_p$

○ Σa_p

☐ Specify notation

● Value

○ Index number

Number of decimals 1

Select 1 axis or 2 axis

● 1 Axis ○ 2 Axis

☐ Display line types into a graph

・ dV_p / dr_p	the area distribution.
・ dV_p / dlog r_p	the volume distribution.
・ ΣV_p	an Integral curve of volume.
・ da_p / dr_p	the length distribution.
・ da_p / dlog r_p	the area distribution.
・ Σa_p	an Integral curve of surface area.

CY plot

Description

As described in "HK plot", Horvath and Kawazoe proposed the theory of slit-shaped micropore distribution. As described in "SF plot", Saito and Foley proposed the theory of cylinder-shaped micropore distribution.

Cheng and Yang applied the theory of HK plot to cage-shaped micropores, enabling analysis of cage-shaped micropore distribution.1)

When cage-shaped micropore radius is L, distance of adsorbate molecule from the center of pore is r, and the number of atoms comprising pore wall is N_1, potential energy $\varepsilon(r)$ is determined by the following equation.

$$\varepsilon(r) = 2\,N_1\,\varepsilon_{12}^{*}\left[-\left(\frac{d_0}{L}\right)^6 \frac{1}{4\left(\frac{r}{L}\right)}\left(\frac{1}{\left(1-\frac{r}{L}\right)^4}-\frac{1}{\left(1+\frac{r}{L}\right)^4}\right)+\left(\frac{d_0}{L}\right)^{12}\frac{1}{10\left(\frac{r}{L}\right)}\left(\frac{1}{\left(1-\frac{r}{L}\right)^{10}}-\frac{1}{\left(1+\frac{r}{L}\right)^{10}}\right)\right] \quad (1)$$

ε_{12}^{*}: Minimum value of potential energy of interaction between adsorbate and adsorbent

d_0: Mean value of adsorbate molecule and adsorbent atom diameter

By considering interaction between adsorbate and adsorbent in the same manner as HK plot, the following equation is obtained.

$$\varepsilon(r) = 2(N_1\,\varepsilon_{12}^{*} + N_2\,\varepsilon_{22}^{*})\left[-\left(\frac{d_0}{L}\right)^6 \frac{1}{4\left(\frac{r}{L}\right)}\left(\frac{1}{\left(1-\frac{r}{L}\right)^4}-\frac{1}{\left(1+\frac{r}{L}\right)^4}\right)+\left(\frac{d_0}{L}\right)^{12}\frac{1}{10\left(\frac{r}{L}\right)}\left(\frac{1}{\left(1-\frac{r}{L}\right)^{10}}-\frac{1}{\left(1+\frac{r}{L}\right)^{10}}\right)\right] \quad (2)$$

Wherein, N_1 is a number of atoms comprising pore wall, and N_2 is a number of molecules of adsorption layer.

$$N_1 = 4\,\pi\,L^2\,N_\mathrm{s} \quad (3)$$

$$N_2 = 4\,\pi\,(L - d_0)^2\,N_\mathrm{A} \quad (4)$$

N_s: Number of adsorbent atoms per unit area, N_A: Number of adsorbate molecules per unit area

Minimum values of potential energy of interaction between adsorbate and adsorbent ε^{*}_{12}, ε^{*}_{22} are obtained as follows:

$$\varepsilon_{12}^{*} = \frac{A_\mathrm{s}}{4\,{d_0}^6} \quad (5)$$

$$\varepsilon_{22}^{*} = \frac{A_\mathrm{A}}{4\,{d_\mathrm{A}}^6} \quad (6)$$

Wherein, A_s and A_A are expressed by the following equation. 2)

$$A_\mathrm{s} = \frac{6\, m\, c^2\, \alpha_\mathrm{s}\, \alpha_\mathrm{A}}{\dfrac{\alpha_\mathrm{s}}{\chi_\mathrm{s}} + \dfrac{\alpha_\mathrm{A}}{\chi_\mathrm{A}}} \tag{7}$$

$$A_\mathrm{A} = \frac{3}{2}\, m\, c^2\, \alpha_\mathrm{s}\, \alpha_\mathrm{A} \tag{8}$$

Through integration of Equation (2) for all pore volume, an equation to define relation between relative pressure and core diameter distribution in CY plot can be obtained.

$$R\,T\,\ln\left(\frac{p}{p_0}\right) = N_\mathrm{Av} \frac{6\,(N_1\, \varepsilon_{12}^{*} + N_2\, \varepsilon_{22}^{*}) L^3}{(L - d_0)^3} \times \left[-\left(\frac{d_0}{L}\right)^6 \left(\frac{1}{12}\, T_1 + \frac{1}{8}\, T_2\right) + \left(\frac{d_0}{L}\right)^{12} \left(\frac{1}{90}\, T_3 + \frac{1}{80}\, T_4\right)\right] \tag{9}$$

$$T_1 = \frac{1}{\left(1 - \dfrac{L - d_0}{L}\right)^3} - \frac{1}{\left(1 + \dfrac{L - d_0}{L}\right)^3} \tag{10}$$

$$T_2 = \frac{1}{\left(1 + \dfrac{L - d_0}{L}\right)^2} - \frac{1}{\left(1 - \dfrac{L - d_0}{L}\right)^2} \tag{11}$$

$$T_3 = \frac{1}{\left(1 - \dfrac{L - d_0}{L}\right)^9} - \frac{1}{\left(1 + \dfrac{L - d_0}{L}\right)^9} \tag{12}$$

$$T_4 = \frac{1}{\left(1 + \dfrac{L - d_0}{L}\right)^8} - \frac{1}{\left(1 - \dfrac{L - d_0}{L}\right)^8} \tag{13}$$

Parameters of adsorbate and adsorbent used for analysis are the same as those for HK plot and SF plot.

≪Reference≫

1) L. S. Cheng, R. T. Yang, Chem. *Eng. Sci.*, **49**, 2599 (1994)
S. U. Rege, R. T. Yang, *AIChE J.*, **46**, 734 (2000)
2) J. G. Kirkwood, *Phys. Zeit.*, **33**, 57 (1932)
A. Muller, *Proc. Roy. Soc.*, **A154**, 624 (1936)

Operation

Operation of analysis software and analysis result

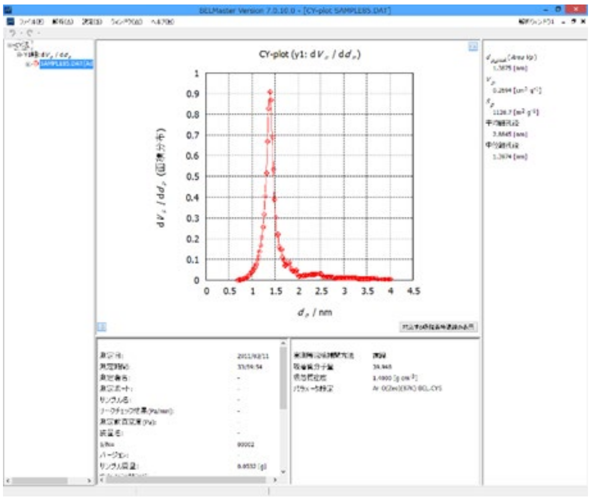
1 Select “Analysis (A)” → “CY plot” in the analysis window menu.

- CY plot analysis is based on adsorption branch data.

→ Operation P.28 “Open file”

2 CY-plot appears as shown on the right.

- The system executes CY plot analysis under preset conditions.
- The figure on the right shows CY-plot of measurement of argon adsorption into zeolite with micropores.



3 This zeolite has many micropores with pore diameter (d_p) of 1 to 2 nm. It can be judged that a peak of distribution is around 1.39 nm.

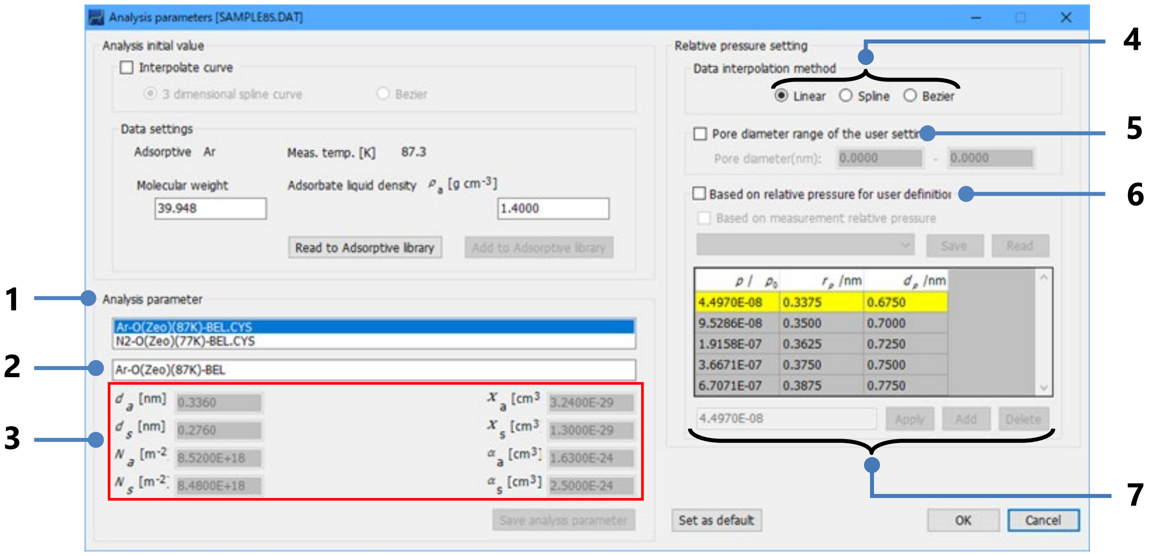
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37
- 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(Zeo)(87K)-BEL.CYS” cannot be changed. Change the name of the file being displayed and then you can change the settings. Click on the OK button. (If “-BEL” is included, the file is not able to save.)


Analysis parameters [SAMPLE85.DAT]

Analysis initial value
☐ Interpolate curve
● 3 dimensional spline curve ○ Bezier

Data settings
Adsorptive Ar
Meas. temp. [K] 87.3
Molecular weight 39.948
Adsorbate liquid density ρ_a [g cm^{-3}] 1.4000

Analysis parameter
Ar-O(Zeo)(87K)-BEL.CYS
N2-O(Zeo)(77K)-BEL.CYS
Ar-O(Zeo)(87K)-BEL

d_a [nm] 0.3360
d_s [nm] 0.2760
N_a [m^{-2}] 8.5200E+18
N_s [m^{-2}] 8.4800E+18
x_a [cm^3] 3.2400E-29
x_s [cm^3] 1.3000E-29
α_a [cm^3] 1.6300E-24
α_s [cm^3] 2.5000E-24

Relative pressure setting
Data interpolation method
● Linear ○ Spline ○ Bezier
☐ Pore diameter range of the user settir
Pore diameter(nm): 0.0000 - 0.0000
☐ Based on relative pressure for user definitio
☐ Based on measurement relative pressure

p/p_0	r_p /nm	d_p /nm
4.4970E-08	0.3375	0.6750
9.5286E-08	0.3500	0.7000
1.9158E-07	0.3625	0.7250
3.6671E-07	0.3750	0.7500
6.7071E-07	0.3875	0.7750

4.4970E-08

1	Set a parameter. ・A parameter can be selected in this field, if any parameter has been registered.
2	A currently selected parameter is displayed. ・If you change the parameter in **3**, it should be changed to any item other than the default setting.
3	The parameter can be changed. ・The parameter name should be changed to any item other than the default setting in **2**. ・For the meaning of each parameter, refer to the following table.
4	Select a file data interpolation method. ・If you conduct curve interpolation of adsorption/desorption isotherm with the same interpolation method, it can be judged whether the interpolation method is proper or not.
5	Specify a calculation range with the pore width. ・If this checkbox is checked, the user-specified pore width is used for calculation. ・When the range is set, the ratio of whole pore volume to the pore volume in the range is calculated automatically.

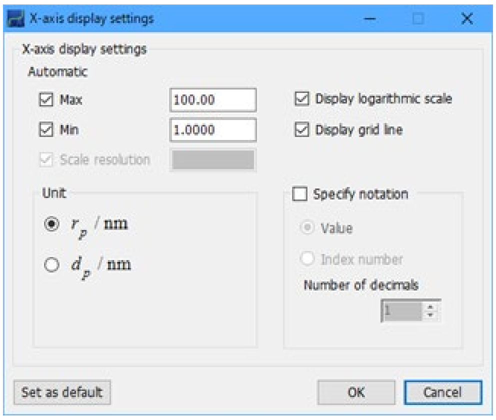
6	Relative pressure data of user definition is used as standard. ・If this checkbox is unchecked, the default point is used for calculation. If this checkbox is checked, the following table can be edited.
7	Edit the relative pressure set value. ・When the [Based on relative pressure of user definition] checkbox is checked, this table can be edited. ・When the checkbox for [Based on measurement relative pressure] is checked, pore diameter is calculated with relative pressure at a measurement point on the adsorption/desorption isotherm. ・Pressing the Alter button changes data in the selected cell (indicated in yellow) to a 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.

Parameter	Adsorbate molecular diameter	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	atoms 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

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

- r_p　　the pore radius.
- d_p　　the pore diameter.



X-axis display settings

X-axis display settings

Automatic

☑ Max 100.00

☑ Min 1.0000

☑ Scale resolution

☑ Display logarithmic scale

☑ Display grid line

Unit

● r_p / nm

○ d_p / nm

☐ Specify notation

○ Value

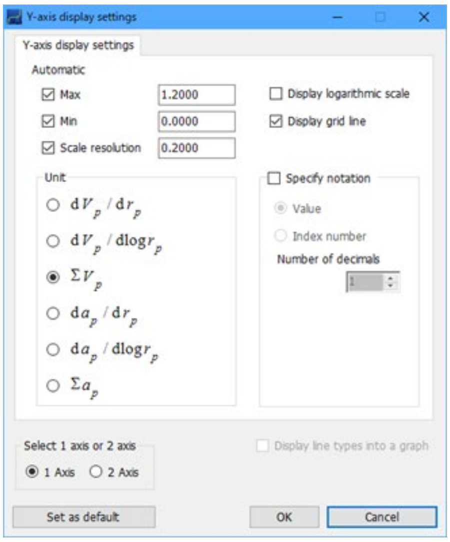
○ Index number

Number of decimals 1

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

• $\mathrm{d}V_p$ / $\mathrm{d}r_p$	the area distribution.
• $\mathrm{d}V_p$ / $\mathrm{dlog}\ r_p$	the volume distribution.
• ΣV_p	an Integral curve of volume.
• $\mathrm{d}a_p$ / $\mathrm{d}r_p$	the length distribution.
• $\mathrm{d}a_p$ / $\mathrm{dlog}\ r_p$	the area distribution.
• Σa_p	an Integral curve of surface area.



☑ Max 1.2000
☑ Min 0.0000
☑ Scale resolution 0.2000
☐ Display logarithmic scale
☑ Display grid line

○ $\mathrm{d}V_p$ / $\mathrm{d}r_p$
○ $\mathrm{d}V_p$ / $\mathrm{dlog}r_p$
● ΣV_p
○ $\mathrm{d}a_p$ / $\mathrm{d}r_p$
○ $\mathrm{d}a_p$ / $\mathrm{dlog}r_p$
○ Σa_p

☐ Specify notation
● Value
○ Index number
Number of decimals 1

● 1 Axis ○ 2 Axis
☐ Display line types into a graph

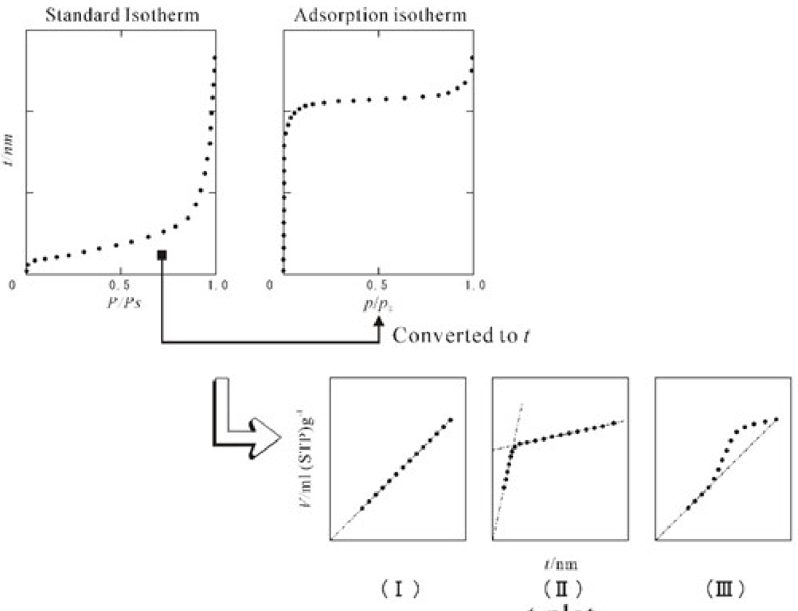
t-plot

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:

$$t = \frac{V_\mathrm{a}}{V_\mathrm{m}} \times 0.354 \ [\mathrm{nm}] \qquad (1)$$

0.354 nm is the thickness of monomolecular layer of nitrogen molecular. 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 Equation (1) converting adsorption isotherm of vertical axis (adsorption amount) to thickness of adsorption layer.



t-plot

isotherm of vertical axis (adsorption amount) to thickness of adsorption layer.

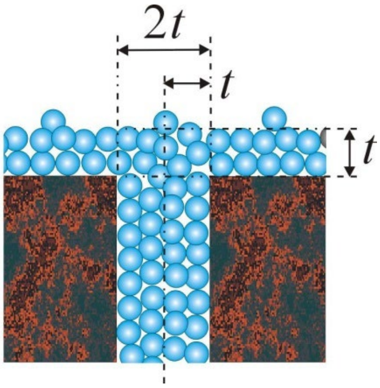
The *t*-plot method, which was invented by Lippens and de Boer, compares the standard isotherm and arbitrary isotherm. Standard isotherm shows the relationship between relative pressure and thickness of adsorption layer. Using standard isotherm, x-axis of isotherm that you wish to analyze can be changed 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 straight line 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 = 0.354 nm) 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.

$$a_s = \frac{s \times 0.354}{22414} \times L \times \sigma = 1.541 \times s \tag{2}$$

Here, L is Avogadro constant and σ is cross-sectional area of adsorbate.



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 straight line L_1 to Equation (1). In the same manner, external surface area (a_2) can be calculated by applying the slope of the other curve L_2 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 L_2 to a volume under liquid condition. Furthermore, adsorption condition is considered to be like in the figure above at intersecting point of L_1 and L_2. Thus, doubled value of t (value 2t) is regarded as the average pore diameter. However, value 2t gives wrong analysis results when pore size is only 2 layers or less. When 2t value is smaller than 0.7 nm, 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 straight line 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, this software contains standard isotherms which are calculated from adsorption isotherm on non-porous material, and standard isotherms 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. We recommend choosing standard isotherm of a material that has similar to your sample in terms of bulk property.

≪Reference≫

・ B. C. Lippens and J. H. de Boer, *J. Catalysis*, **4**, 319 (1965).

Operation

Operation of analysis software and analysis result

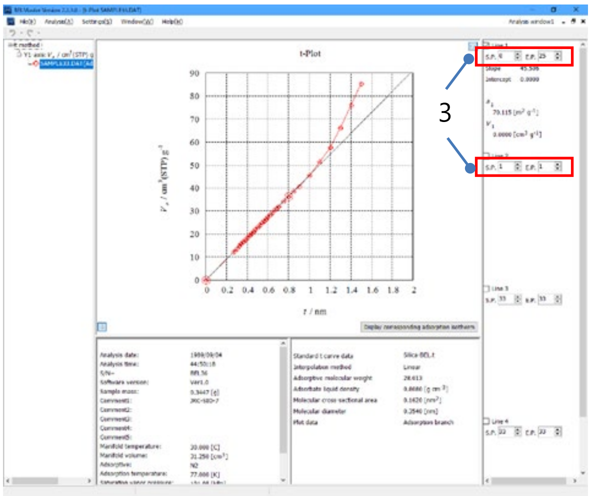
1 Select "Analysis(A)" and then "*t* plot" from the analysis window menu.

- The software will execute *t*-plot calculations from the adsorption or desorption data of an adsorption isotherm.

→ Operation P.28 "Open file"

2 A *t*-plot is displayed as shown right. The software will automatically draw two straight lines.

- The figure on the right is a *t*-plot of a nitrogen isotherm for macroporous silica. "silica-BEL.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.

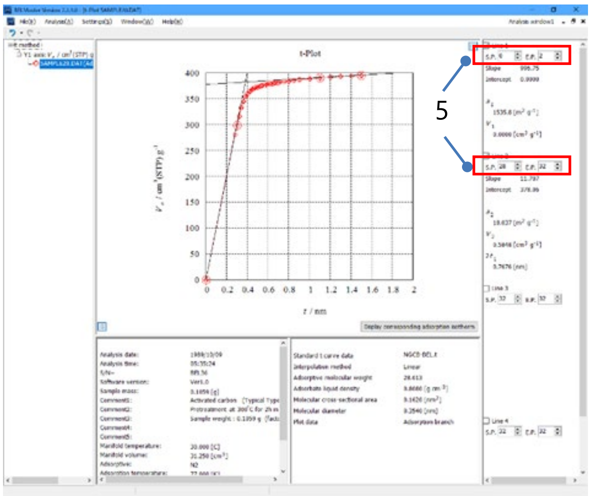


3 Select a start point (normally the zero position) and an end point for the first straight line. From the slope of this line, the specific surface area (a_1) 70.1 m^2 g^{-1} is calculated. This value is a good match for the 70.0 m^2 g $^{-1}$ obtained from the BET-plot (P. 91). The 2nd straight line is not needed. Set the the starting and end points as the same point and delete the line.

- The default starting and end points of the 1st and 2nd lines are the “minimum data point (zero position)” and the “minimum data +1”. The starting and end points of the 3rd and 4th line are the “maximum data point -1” and the “maximum data point”.
- If the second line is unchecked, the third and fourth lines are automatically unchecked, so that these lines are not displayed. This also applies to the third line.

4 The figure on the right is a t-plot of a nitrogen isotherm for microporous activated carbon.

- “NGCB-BEL.t” was specified as the standard isotherm.



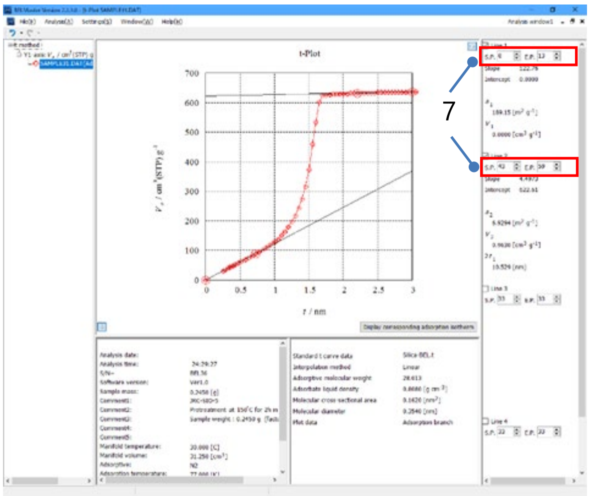
5 Select a starting point (normally the zero position) and end point of the first straight line. The software will calculate the specific surface area (a_1) 1,536 m^2 g^{-1} from the slope of this straight line. Select the starting and end points of the 2nd line.

- The default starting and end points of the 1st and 2nd lines are the “minimum data point (zero position)” and the “minimum data +1”. The star ting and end points of the 3rd and 4th line are the “maximum data point -1” and the “maximum data point”.

Using the slope of this straight line, the external surface area (a_2) 18 m^2 g^{-1} can be obtained. The volume (V_2) of micropores 0.585 cm^3 g^{-1} can be calculated from the intercept. A micropore area of 1,532 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 0.76 mm and this value is a good match for the peak value of the pore width obtained from the MP-plot.

6 The figure on the right is a *t*-plot of a nitrogen isotherm for mesoporous silica.

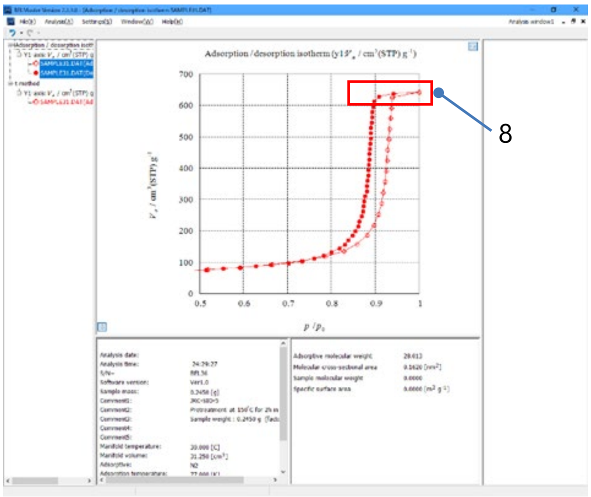
- "silica-BEL.t" is used as a standard isotherm.
  The [Based t data for user definition] was clicked on and the calculation range was widened to 3 nm.



7 Select a starting point (normally the zero position) and an end point of the 1st straight line. The software will calculate the specific area (a_1) as 189 m^2 g^{-1} from the slope of this line.

- The default starting and end points of the 1st and 2nd lines are the "minimum data point (zero position)" and the "minimum data +1". The starting and end points of the 3rd and 4th line are the "maximum data point -1" and the "maximum data point".

8 If the adsorption amount 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) 7 m^2 g^{-1}can be obtained from the slope of this line and the mesopore volume (V_2) 0.963 cm^3 g^{-1} is calculated from the intercept. The mesopore area can be obtained as 182 m^2 g^{-1}, from a_1 - a_2.



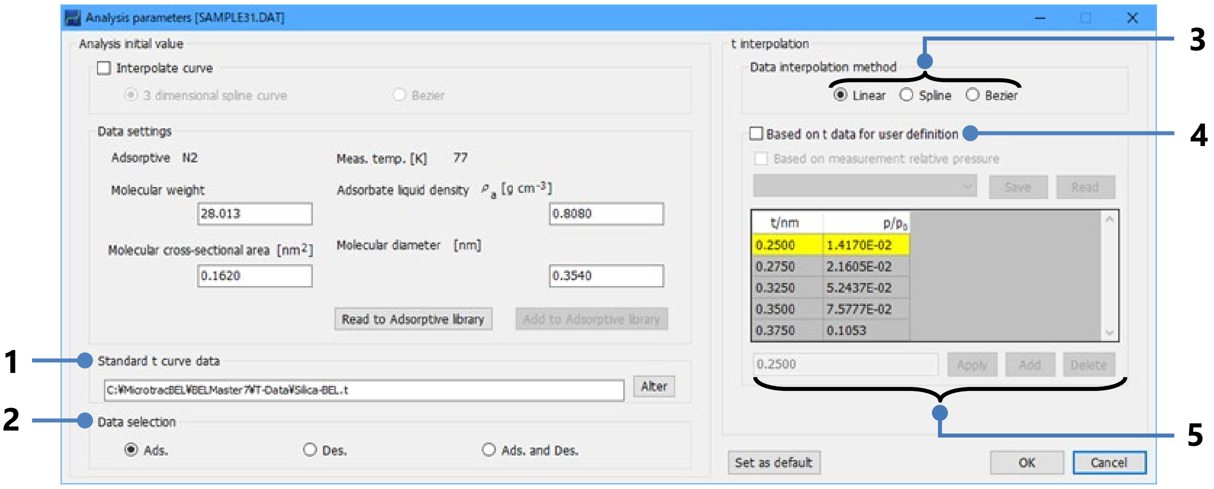
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



Analysis parameters [SAMPLE31.DAT]

Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Data settings

Adsorptive N2

Meas. temp. [K] 77

Molecular weight 28.013

Adsorbate liquid density ρ_a [g cm^{-3}] 0.8080

Molecular cross-sectional area [nm^2] 0.1620

Molecular diameter [nm] 0.3540

Standard t curve data

C:¥MicrotracBEL¥BELMaster7¥T-Data¥Silica-BEL.t

Data selection

● Ads. ○ Des. ○ Ads. and Des.

t interpolation

Data interpolation method

● Linear ○ Spline ○ Bezier

☐ Based on t data for user definition

☐ Based on measurement relative pressure

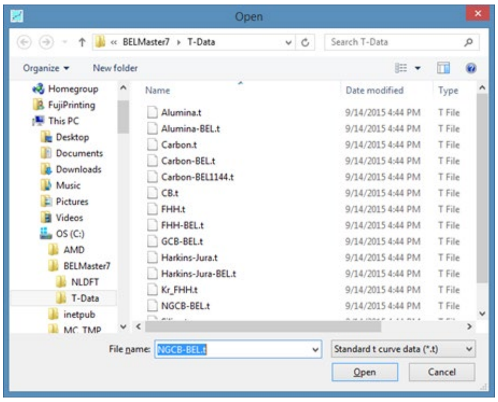
t/nm	p/p_0
0.2500	1.4170E-02
0.2750	2.1605E-02
0.3250	5.2437E-02
0.3500	7.5777E-02
0.3750	0.1053

0.2500

---

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.



Open

« BELMaster7 › T-Data

Name	Date modified	Type
Alumina.t	9/14/2015 4:44 PM	T File
Alumina-BEL.t	9/14/2015 4:44 PM	T File
Carbon.t	9/14/2015 4:44 PM	T File
Carbon-BEL.t	9/14/2015 4:44 PM	T File
Carbon-BEL1144.t	9/14/2015 4:44 PM	T File
CB.t	9/14/2015 4:44 PM	T File
FHH.t	9/14/2015 4:44 PM	T File
FHH-BEL.t	9/14/2015 4:44 PM	T File
GCB-BEL.t	9/14/2015 4:44 PM	T File
Harkins-Jura.t	9/14/2015 4:44 PM	T File
Harkins-Jura-BEL.t	9/14/2015 4:44 PM	T File
Kr_FHH.t	9/14/2015 4:44 PM	T File
NGCB-BEL.t	9/14/2015 4:44 PM	T File

File name: NGCB-BEL.t

Standard t curve data (*.t)

2 Select which data will be used for calculation, the adsorption branch, desorption branch or both.

- When the adsorption branch of the adsorption/desorption isotherm is not saturated, t-plot with the desorption isotherm may be suitable for calculation of outer surface area.
- When six pieces or more data are displayed, adsorption/desorption cannot be selected.

3 If interpolation method is not selected, the software will calculate a *t*-plot at the default setting point.

- When any method is selected, the software will calculate the *t*-value specified in the table below.

4 *t*-data setting.

- This table can be edited when you click on [Based on t data for user definition].
- In the case the pressure measured in the data file is used, click on [Based on measurement relative pressure] and select the data in the pull-down menu.

5	Edit the relative pressure set value. ・When the [Based on t data for user definition] checkbox is checked, this table can be edited. ・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 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. ・In the case the pressure measured in the data file is used, click on [Based on measurement relative pressure] and select the data in the pull down menu.

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

α_s plot

Description

Like t plot, α_s plot calculates specific surface area of sample by comparing isotherm of standard sample and isotherm of the sample.

$$t = \frac{V_a}{V_m} \times 0.354\ [\mathrm{nm}] \qquad (1)$$

t value, which is calculated from standard isotherm and is used in t plot, indicates the thickness of adsorbate layer, but the reliability of the numerical value will be lost when $2t$ is below 0.7 nm.

t value was originally invented to calculate the thickness of adsorbate 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 adsorbate layer thickness and monolayer amount adsorbed V_m are not necessary. Also, when single molecular layer is not formed or when BET-plot does not come into effect, monolayer amount adsorbed cannot be calculated and it is impossible to use t plot.

In order to solve the problem of t plot, 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 N_2 adsorption isotherm at 77 K of standard sample) rather than by standardization with t value. [1) 2)]

$$\alpha_s = \frac{V_a}{V_a\ (p / p_0 = 0.4)} \qquad (2)$$

V_a indicates adsorption amount at arbitrary equilibrium pressure.

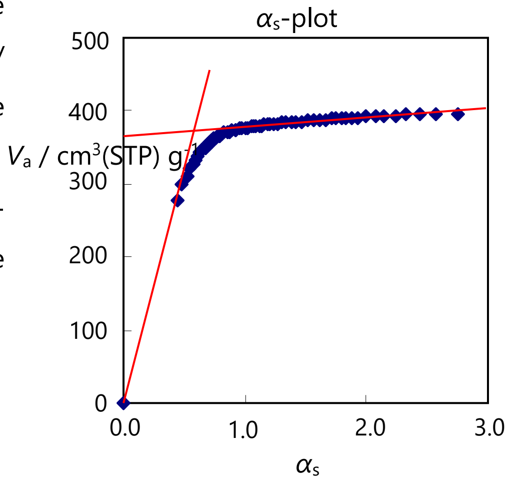
The reason that relative pressure for standardization was set to 0.4 is due to the following reasons:

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 (2), and then α_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 straight line slope.



The slope of α_s-plot of standard sample is calculated, which is b_α(standard). Also, the slope of the first straight line is calculated from α_s-plot of analysis sample, which is b_α(test).

The ratio between the above mentioned b_α(standard) and b_α(test) is equal to the ratio between two specific surface areas. Therefore, if standard sample specific surface area is expressed by a_s(standard) and sample specific surface area is expressed by a_s(test),

$$\frac{b_\alpha\ (\mathrm{test})}{b_\alpha\ (\mathrm{standard})} = \frac{n_{0.4}\ (\mathrm{test})}{n_{0.4}\ (\mathrm{standard})} = \frac{\alpha_s\ (\mathrm{test})}{\alpha_s\ (\mathrm{standard})} \qquad (3)$$

thus

$$\alpha_s\ (\mathrm{test}) = \frac{b_\alpha\ (\mathrm{test})}{b_\alpha\ (\mathrm{standard})} \times \alpha_s\ (\mathrm{standard}) \qquad (4)$$

b_α(standard) and a_s(standard) are already known in this case, thus

$$k = \frac{\alpha_s\ (\mathrm{standard})}{b_\alpha\ (\mathrm{standard})} \qquad (5)$$

$$\alpha_s\ (\mathrm{test}) = b_\alpha\ (\mathrm{test}) \times k \qquad (6)$$

Whole specific surface area a_1 [$\mathrm{m^2\ g^{-1}}$] of the sample can be calculated with (6).

External surface area a_2 [$\mathrm{m^2\ g^{-1}}$] and pore volume V_p [$\mathrm{cm^3\ g^{-1}}$] can be calculated from the slope of the second straight line 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 "*t-plot*").

Unlike *t* plot, in α_s-plot, the average pore radius cannot be worked out from the intersecting point of the 2 straight line 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_p) = whole surface area - external surface area $a_p = a_1 - a_2 = 2 \pi r L$ [2]

From [1] and [2], pore radius is calculated as follows.

$$r = \frac{2\,V_p}{a_p} = \frac{2\,V_p}{a_1 - a_2} \qquad (7)$$

In *t* plot, it is impossible to evaluate pore size below 0.35 nm because there would be no physical meaning when *t* value is below 0.35 nm. 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 straight line can be drawn easily because plot can be obtained even when α_s -value is small. Also, the first straight line has to pass the original point in *t* plot, but in α_s -plot it is possible to select the range without the fixed original point so that straight line 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). This analysis software contains standard isotherms that are made from adsorption isotherm on non-porous material. 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-sectional area of adsorptive.

≪Reference≫

・ D. Atkinson, A. I. McLeod, K. S. W. Sing, *J. Chim. Phys.*, **81**, 791 (1984).

・ K. S. W. Sing, *Carbon*, **27**, 5 (1989).

Operation

Operation of analysis software and analysis result

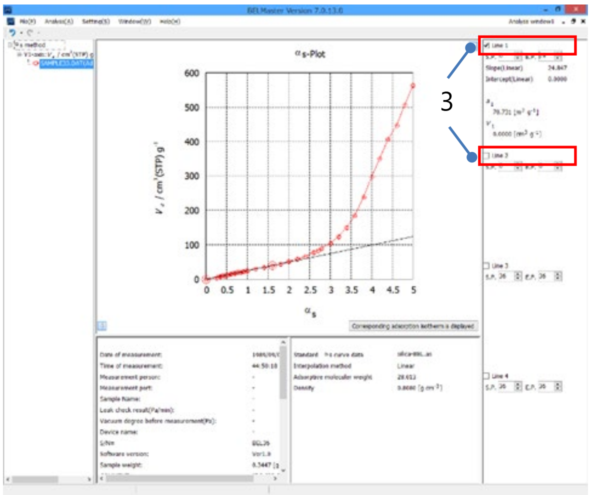
1 Select "Analysis(A)" and then "*t* plot" from the analysis window menu.

- The software will execute an α_s plot from adsorption data of an isotherm.

→ Operation P.28 "Open file"

2 An α_s-plot is displayed as shown right. The software automatically draws two straight lines.

- The figure on the right is an α_s-plot of a nitrogen adsorption isotherm for macroporous silica. "Silica-BEL.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.



3

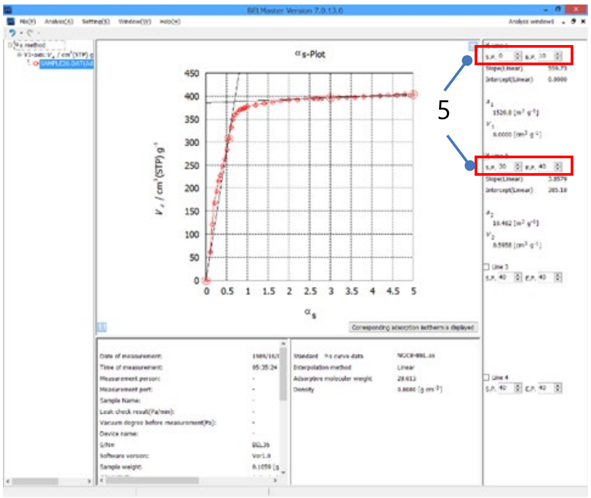
Select a starting point (normally the zero position) and end point of the first straight line. The specific area (a_1) 70.7 m^2 g^{-1} is calculated from the slope of this line. The 2nd straight line is not needed. Use the same point as both the starting and end points and delete the straight line.

- As a default, the starting and end points of the 1st and 2nd lines are the "zero position" and the "first point", and the starting and end points of the 3rd and 4th line are the "maximum data point -1" and the "maximum data point".
- If the second line is unchecked, the third and fourth lines are automatically unchecked, so that these lines are not displayed. This also applies to the third line.

4

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.



5

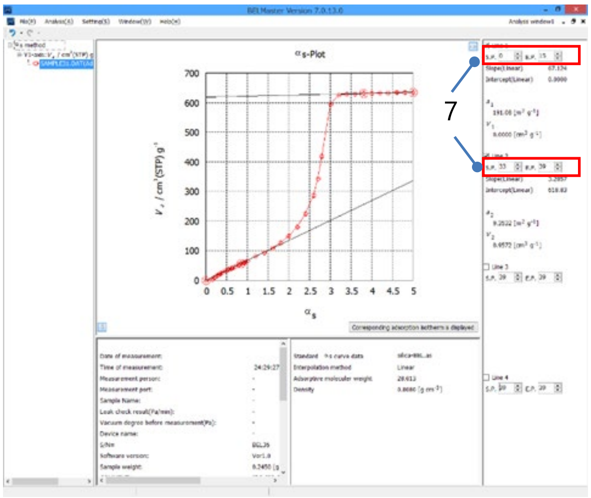
Select a starting point (normally the zero position) and end point of first the straight line. From the slope of this straight line, the software will calculate the specific area (a_1) 1,520 m^2 g^{-1}. Select the starting and end points of the 2nd line.

- As a default, the starting and end points of the 1st and 2nd lines are the "zero position" and the "first point", and the starting and end points of the 3rd and 4th line are the "maximum data point -1" and the "maximum data point".

The external surface area (a_2) 10.5 m^2 g^{-1} can be obtained using the slope of this straight line. The volume (V_2) of the micropores 0.596 cm^3 g^{-1} can be calculated from the intercept. The pore area of the micropores is obtained as 1,510 m^2 g^{-1}, from (a_1 - a_2).

6 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.



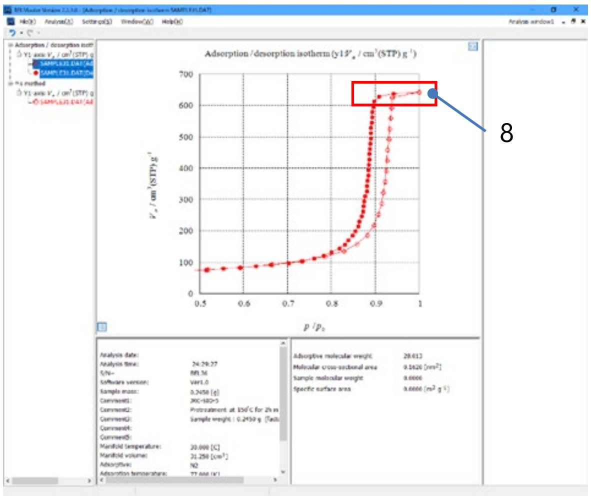
7 Select a starting point (normally the zero position) and an end point for the 1st straight line.The software will calculate the specific area (a_1) 191 m^2 g^{-1} from the slope of this line.

- As a default, the starting and end points of the 1st and 2nd lines are the "zero position" and the "first point", and the starting and end points of the 3rd and 4th line are the "maximum data point -1" and the "maximum data point".

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.

Select the starting and end points of the 2nd straight line. From the slope of this line, the external surface area (a_2) 9.4 m^2 g^{-1} can be obtained. The mesopore volume (V_2).

0.957 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).



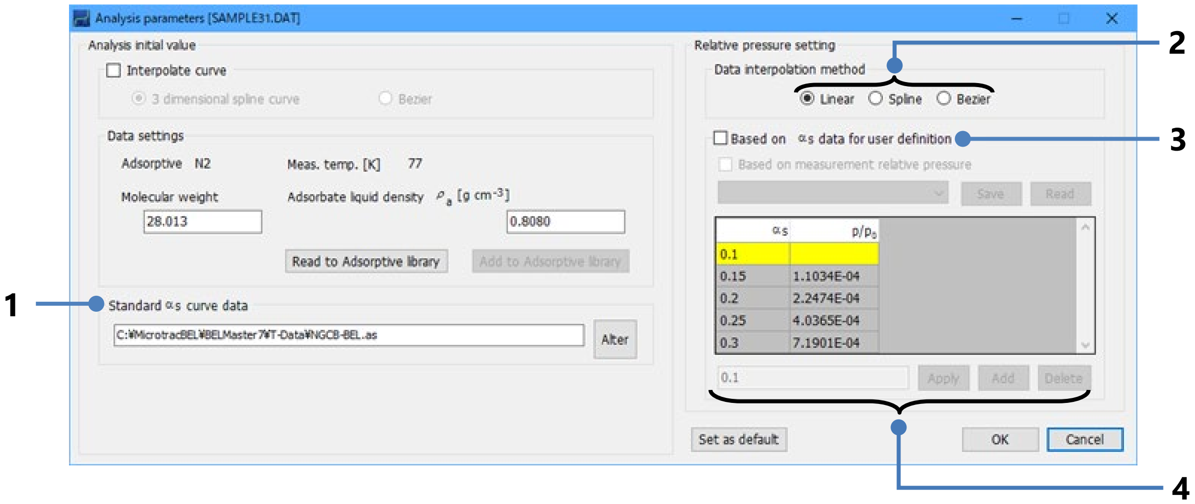
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37



Analysis parameters [SAMPLE31.DAT]

Analysis initial value

☐ Interpolate curve

○ 3 dimensional spline curve　○ Bezier

Data settings

Adsorptive　N2　　Meas. temp. [K]　77

Molecular weight　28.013

Adsorbate liquid density ρ_a [g cm^{-3}]　0.8080

Standard αs curve data　C:¥MicrotracBEL¥BELMaster7¥T-Data¥NGCB-BEL.as

Relative pressure setting

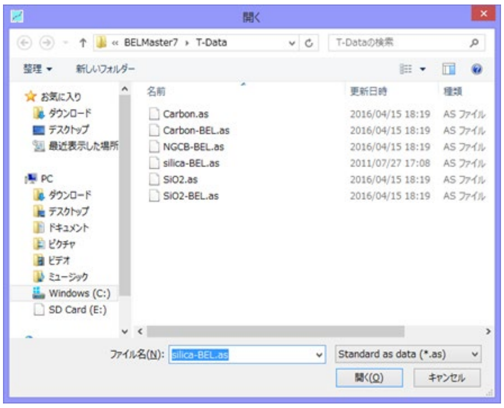
Data interpolation method　● Linear　○ Spline　○ Bezier

☐ Based on αs data for user definition

☐ Based on measurement relative pressure

αs	p/p$_0$
0.1	
0.15	1.1034E-04
0.2	2.2474E-04
0.25	4.0365E-04
0.3	7.1901E-04

0.1

1	Select a standard α_s -curve. ・Select a standard isotherm that has similar chemical characteristics to the sample surface. ・Click on the Alter button. The right selection window will appear. Select a standard α_s -curve file and click on the Open button.  開く « BELMaster7 › T-Data ファイル名(N): silica-BEL.as　Standard as data (*.as) 名前 / 更新日時 / 種類: Carbon.as 2016/04/15 18:19 ASファイル; Carbon-BEL.as 2016/04/15 18:19 ASファイル; NGCB-BEL.as 2016/04/15 18:19 ASファイル; silica-BEL.as 2011/07/27 17:08 ASファイル; SiO2.as 2016/04/15 18:19 ASファイル; SiO2-BEL.as 2016/04/15 18:19 ASファイル
2	If interpolation method is not selected, the software will calculate a t-plot at the default setting point. ・When any method is selected, the software will calculate the t-value specified in the table below.
3	α_s setting ・When [Based on α_s data for user definition] is selected, this table can be edited.

4 Edit the α_s setting.

- When the [Based on α_s data for user definition] is checked, this table can be edited.
- When the [Based on measurement relative pressure] is checked, α_s -plot is executed with relative pressure at a measured point on the adsorption/desorption isotherm.
- 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.

➢ X axis display settings

Select "Settings(S)" → "X axis display settings(X)" to select desired unit of X axis.

➢ Y axis display settings

Select "Settings(S)" → "Y axis display settings(Y)" to select desired unit of Y axis.

DA plot

Description

In 1960, Dubinin and Radushkevich introduced DR equation that they derived from adsorption potential theory of Polanyi. Polanyi hypothesized that pressure of adsorbate is equal to the saturation vapor pressure p_0 of its gas. Expressing pressure of adsorptive (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.

$$\varepsilon = R\,T\,\ln\frac{p_0}{p} \qquad (1)$$

Polanyi defined ε as adsorption potential. ε can be replaced by Gibbs free energy change $-\Delta G$ at adsorption.

$$\varepsilon = -\Delta G \qquad (2)$$

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.

$$\theta = \frac{V}{V_\mathrm{p}} \qquad (3)$$

V_p indicates whole micropore volume, V means pore volume filled by adsorbate at relative pressure p / p_0. θ is also the function of relative pressure thus the function of ε from Equation (3).

$$\theta = f\left(\frac{\varepsilon}{\beta}\right) \qquad (4)$$

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.

$$\theta = \exp\left[-k\left(\frac{\varepsilon}{\beta}\right)^2\right] \qquad (5)$$

k is a constant number that depends on pore structure. The following equation is obtained from Equation (3), (4) and (5).

$$V = V_\mathrm{p}\exp\left[-\frac{\varepsilon}{\beta^2}\left(R\,T\,\ln\frac{p_0}{p}\right)^2\right] \qquad (6)$$

or,

$$\frac{V}{V_\mathrm{p}} = \exp\left[-B\left(\frac{T}{\beta}\right)^2 \log_{10}{}^2\frac{p_0}{p}\right] \qquad (7)$$

where B is a constant represented by Equation (8).

$$B = 2.303\,\frac{R^2}{k} \qquad (8)$$

Equation (7) can be coverted to

$$\log_{10} V \;=\; \log_{10} V_{\mathrm{p}} - C\ \log_{10}{}^{2} \frac{p_0}{p} \tag{9}$$

where

$$C \;=\; B \left(\frac{T}{\beta}\right)^{2} \tag{10}$$

Equation (6), (7) and (9) are called DR equation. If you convert adsorption amount to V using adsorbate liquid density, and then plot $\log_{10} V_{\mathrm{p}}$ against $\log_{10}^{2}\left(p_0 / p\right)$ (DR-plot), you will get a straight line with the intercept $\log_{10} V_{\mathrm{p}}$ 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.

$$\theta \;=\; \exp\left[-\left(\frac{R\,T}{\varepsilon}\right)^{n}\ \ln^{2}\frac{p_0}{p}\right] \tag{11}$$

or,

$$\log_{10} V \;=\; \log_{10} V_{\mathrm{p}} - C'\ \log_{10}{}^{n} \frac{p_0}{p} \tag{12}$$

where C' can be given by Equation (13).

$$C' \;=\; 2.303^{n-1} \left(\frac{R\,T}{\epsilon}\right)^{n} \tag{13}$$

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 $\log_{10}^{n}\left(p_0 / p\right)$. n is a small integral number (normally 1 to 3). Kawazoe et al. categorized adsorbate molecule diameters expressing adsorbate molecule diameter as d and pore size as D like the following table. Applying n = 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 plot is often used for calculation of pore volume. If plots make straight line, 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 plot does not have to be limited to integral number in theory.

≪Reference≫

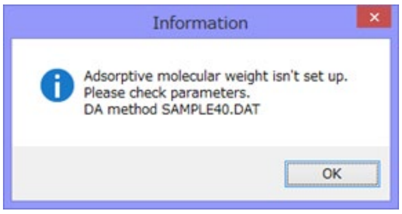
- M. M. Dubinin, *Chem. Rev.*, **60**, 235 (1960)
  D. H. Everett, J. C. Powl, *J. Chem. Soc., Faraday Trans. 1*, **72**, 619 (1976)
- B. P. Bering, M. M. Dubinin, and V. V. Serpinsky, *J. Colloid Interface Sci.*, **21**, 378 (1966)
  A. Saito, H. Foley, *Microporous Mater.*, **3**, 531 (1995).

Operation

Operation of analysis software

1 Select “Analysis(A)” and then “DA plot” from the analysis window menu.

- The software will execute a DA plot from the adsrotption data of an isotherm.
- If adsorptive molecular weight or density has not been entered, the window shown on the right will appear. Click on the OK button and the analysis parameter window will open. Enter an adsorptive molecular weight or density.

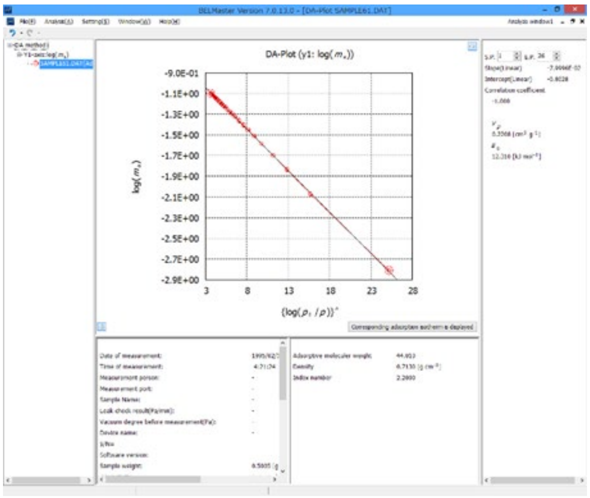


Adsorptive molecular weight isn't set up.
Please check parameters.
DA method SAMPLE40.DAT

→ Operation P.28 “Open file”

2 A DA-plot is displayed as shown right. A regression line is drawn between the 1st point and the last point.

- The figure on the right shows a DA-plot of carbon dioxide adsorption isotherm for microporous activated carbon.



3 Select the starting and end points of a straight line.

- If the “Index number” is not appropriate, the linearity will decrease. Open the “Analysis parameter” window by selecting “Settings(S)” and then the “Analysis parameters settings(A)” menu. Then, enter an appropriate “Index number”.

About analysis result

The software 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 upper right figure is specific mass adsorbed on 1 g adsorbent.

V_p / cm^3 g^{-1} expressed as follows.

$$V = \frac{m_\mathrm{a}}{\rho_\mathrm{a}} \qquad V = \frac{10^i}{\rho_\mathrm{a}}$$

where ρ_a is adsorbate liquid density, i is the slope of straight line.

After entering an "index number" of 2.2, good linearity was obtained. The pore volume 0.221 cm^3 g^{-1} and adsorption potential 12.3 kJ mol^{-1} were obtained from the slope and intercept.

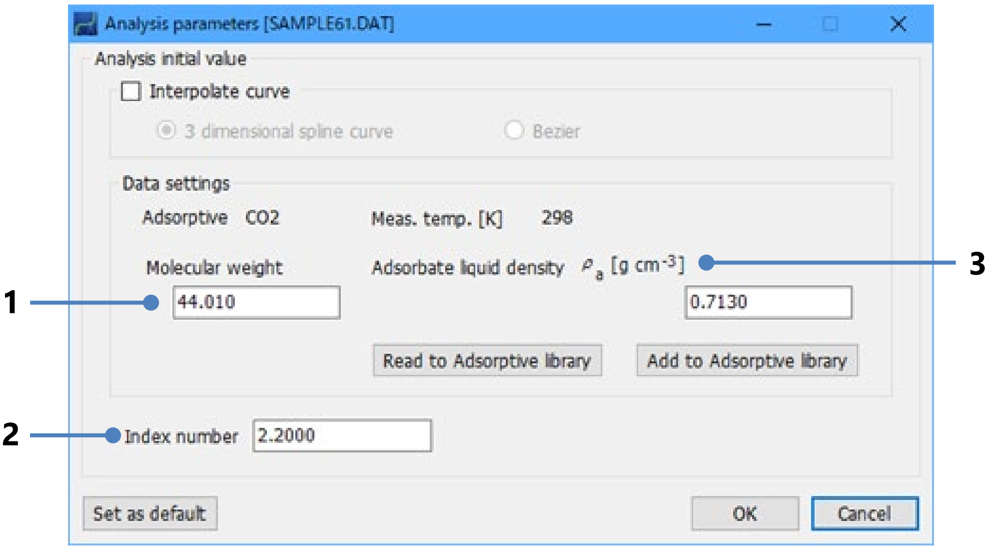
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37.



Adsorptive CO2

Meas. temp. [K] 298

Molecular weight 44.010

Adsorbate liquid density ρ_a [g cm^{-3}] 0.7130

Index number 2.2000

1	Enter a molecular weight of the adsorptive.
2	Enter an index number (real number 0 to 10).
3	Enter an adsorbate liquid density (g cm^{-3}).

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

Metal dispersion analysis

Description

Metal dispersion can be calculated from gas adsorption amount (chemisorption volume) as follows. Adsorption amount value used in this calculation is given as gas volume of standard condition V [$\mathrm{cm^3(STP)\ g^{-1}}$].

N_g, the number of moles of the gas that adsorobed on supported metal catalyst 1 g is expressed as bellow.

$$N_\mathrm{g} = \frac{V}{22414} \tag{1}$$

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).

$$N_\mathrm{s} = k_\mathrm{sf} \times N_\mathrm{g} = k_\mathrm{sf} \times \frac{V}{22414} \tag{2}$$

wt % of supported metal content is *c* %. The number of moles of metal atom per catalyst 1 g, N_T, can be calculated from the following equation.

$$N_\mathrm{T} = \frac{c}{M} \times \frac{1}{100} \tag{3}$$

Here, *M* indicates atomic weight of supported metal atom.

Therefore, metal dispersion D_m can be calculated by the following equation.

$$D_\mathrm{m} = \frac{N_\mathrm{s}}{N_\mathrm{T}} = \frac{k_\mathrm{sf} \times 100 \times M \times V}{22414 \times c} \tag{4}$$

a_s (Sample) [$\mathrm{m^2\ g^{-1}}$], supported metal surface area per catalyst 1 g can be calculated by the following.

$$a_\mathrm{s}(\mathrm{Sample}) = \frac{k_\mathrm{sf} \times V \times 6.022 \times 10^{23}}{22414} \times a_\mathrm{m} \times 10^{-18} \tag{5}$$

Also, a_s (Metal) [$\mathrm{m^2\ g^{-1}}$], supported metal surface area per supported metal 1 g can be calculated by the following.

$$a_\mathrm{s}(\mathrm{Metal}) = \frac{a_\mathrm{s}(\mathrm{Sample}) \times 100}{c} \tag{6}$$

a_m [$\mathrm{nm^2\ atom^{-1}}$] is the cross-sectional area that a supported metal atom occupies (supported metal cross section area).

Suppose supported metal particle is cubic, the average metal particle size l_m [nm] is,

$$l_\mathrm{m} = \frac{6}{\rho \times a_\mathrm{s}(\mathrm{Metal})} \times 10^3 \tag{7}$$

where ρ [$\mathrm{g\ cm^{-3}}$] 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, P. 261).

Supported metal		Atomic weight	Density / g cm^{-3}	Metal cross section area / nm2·$atom^{-1}$
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

≪Reference≫

- Edited by Catalysis Society of Japan, Catalysis course (supplementary volume), Catalysis experiment hand book, P. 261 Japanese edition

Operation

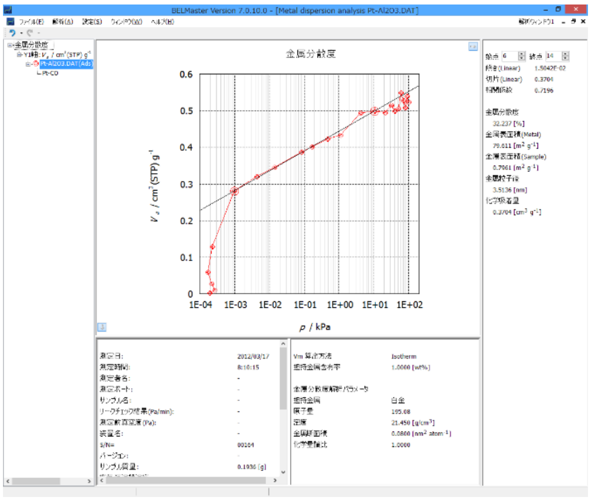
Operation of analysis software

1 Select “Analysis(A)” and then “Metal dispersion analysis” from the analysis window menu.

- The software will execute a metal dispersion analysis from adsorption data of isotherms.

→ Operation P.28 “Open file”

2 The metal dispersion graph is displayed as shown to the right, and an approximate straight line is drawn automatically.



始点 6 終点 14
傾き(Linear) 1.5042E-02
切片(Linear) 0.3704
相関係数 0.7196

金属分散度 32.237 [%]
金属表面積(Metal) 79.611 [m^2 g^{-1}]
金属表面積(Sample) 0.7961 [m^2 g^{-1}]
金属粒子径 3.5136 [nm]
化学吸着量 0.3704 [cm^3 g^{-1}]

測定日: 2012/03/17
測定時間: 8:10:15
測定者名: -
測定ポート: -
サンプル名: -
リークチェック結果(Pa/min): -
測定前真空度(Pa): -
装置名: -
S/N= 00104
バージョン: -
サンプル質量: 0.1936 [g]

Vm 算出方法 Isotherm
担持金属含有率 1.0000 [wt%]

金属分散度解析パラメータ
担持金属 白金
原子量 195.08
密度 21.450 [g/cm^3]
金属断面積 0.0800 [nm^2 atom^{-1}]
化学量論比 1.0000

3 Select the starting and end points of an approximate curve.

4 The supported metal content (%), stoichiometry factor, slope of the approximate curve, intercept, correlation coefficient,

metal dispersion (%)

metal surface area (Metal) (m^2 g^{-1})

metal surface area (Sample) (m^2 g^{-1})

average metal particle size (nm), and

chemisorption volume (cm^3 g^{-1}) will be displayed.

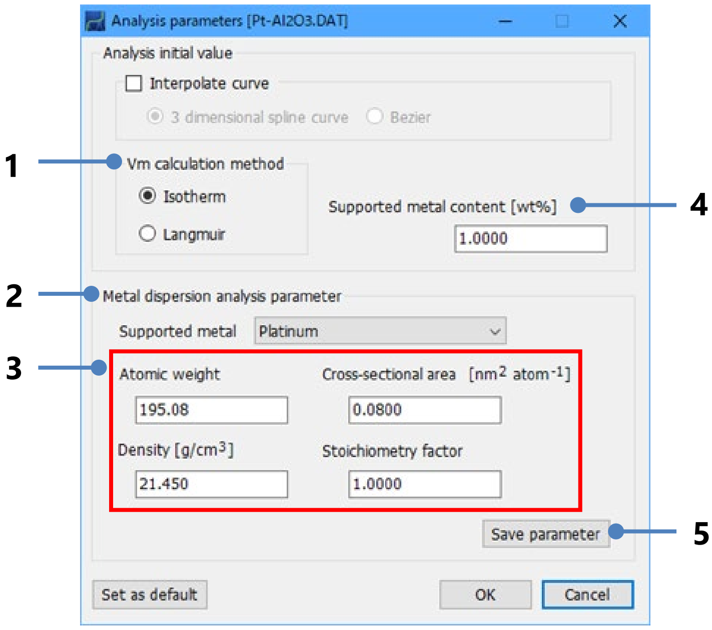
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37.



☐ Interpolate curve
● 3 dimensional spline curve ○ Bezier

● Isotherm
○ Langmuir

Supported metal content [wt%]: 1.0000

Supported metal: Platinum

Atomic weight: 195.08

Cross-sectional area [nm^2 atom^{-1}]: 0.0800

Density [g/cm^3]: 21.450

Stoichiometry factor: 1.0000

1	Select method for calculating the chemisorption volume.
2	Select a supported metal. The parameters previously stored are displayed.
3	Enter the atomic weight, metal cross section area, density, and a stoichiometry factor.
4	Enter a supported metal content.
5	After changing the parameters, click on the Save parameter button, the parameter data will be overwritten in the stored data.

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

Isosteric heat of adsorption

Description

Adsorption involves exothermic phenomenon. 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 exothermic. q_{diff} which is expressed by the following equation is called differential heat of adsorption.

$$q_{\mathrm{diff}} = \frac{\mathrm{d}Q}{\mathrm{d}n_{\mathrm{a}}} \tag{1}$$

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.

$$G_{\mathrm{a}} = G_{\mathrm{g}} \tag{2}$$

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:

$$\mathrm{d}G_{\mathrm{a}} = -S_{\mathrm{a}}\,\mathrm{d}T + V_{\mathrm{a}}\,\mathrm{d}P \tag{3}$$

$$\mathrm{d}G_{\mathrm{g}} = -S_{\mathrm{g}}\,\mathrm{d}T + V_{\mathrm{g}}\,\mathrm{d}P \tag{4}$$

n_{a} is constant, thus

$$\mathrm{d}G_{\mathrm{a}} = \mathrm{d}G_{\mathrm{g}} \tag{5}$$

The following equation can be derived from (2), (3) and (4)

$$\left(\frac{\partial P}{\partial T}\right)_{n_{\mathrm{a}}} = \frac{S_{\mathrm{g}} - S_{\mathrm{a}}}{V_{\mathrm{g}} - V_{\mathrm{a}}} \tag{6}$$

Applying $V_{\mathrm{g}} = RT / P$ ($V_{\mathrm{g}} \gg V_{\mathrm{a}}$) from the state equation of ideal gas, the above equation becomes as follows.

$$\left(\frac{\partial \ln P}{\partial T}\right)_{n_{\mathrm{a}}} = \left(S_{\mathrm{g}} - S_{\mathrm{a}}\right) R\,T = -\frac{\Delta S_{\mathrm{ads}}}{R\,T} \tag{7}$$

Suppose $S_{\mathrm{g}} - S_{\mathrm{a}} = \Delta S_{\mathrm{ads}}$. At equilibrium state, enthalpy change caused by adsorption ΔH_{ads} has the following relation with absolute temperature and entropy.

$$\left(\frac{\partial \ln P}{\partial T}\right)_{n_{\mathrm{a}}} = \left(S_{\mathrm{g}} - S_{\mathrm{a}}\right) R\,T = -\frac{\Delta S_{\mathrm{ads}}}{R\,T} \tag{8}$$

Following Equation (Clausius-Clapeyron equation) can be obtained from Equation (7).

$$\left(\frac{\partial \ln P}{\partial T}\right)_{n_{\mathrm{a}}} = \left(S_{\mathrm{g}} - S_{\mathrm{a}}\right) R\,T = -\frac{\Delta S_{\mathrm{ads}}}{R\,T} \tag{9}$$

$-\Delta H_{\mathrm{ads}}$ is isosteric enthalpies of adsorption q_{st}. The relation between q_{st} and q_{diff} is as follows.

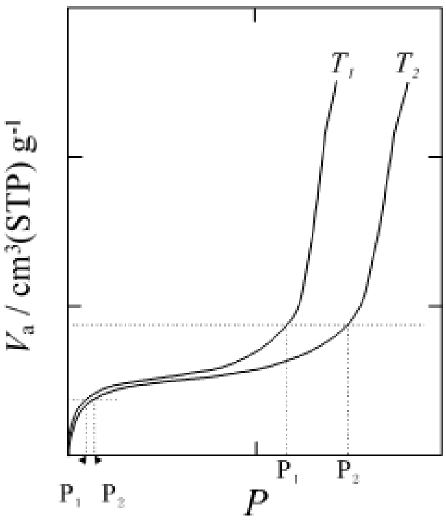
$$q_{\mathrm{st}} = q_{\mathrm{diff}} + R\,T \tag{10}$$

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.

This 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).

$$q_{\mathrm{st}} = \frac{R\,T_1\,T_2}{T_2 - T_1}(\ln P_2 - \ln P_1) \tag{11}$$

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 chemisorption etc.



Operation

Operation of analysis software

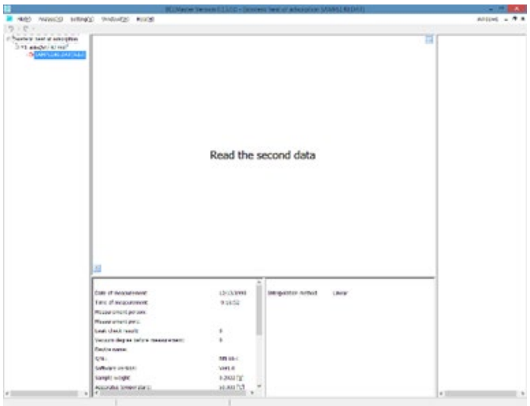
1 Select “Analysis(A)” and then “Isosteric heat of adsorption” from the analysis window menu.

- The software will execute an isosteric heat of adsorption analysis from adsorption branch of the isotherm.
- This analysis reads two data files measured at different adsorption temperatures.

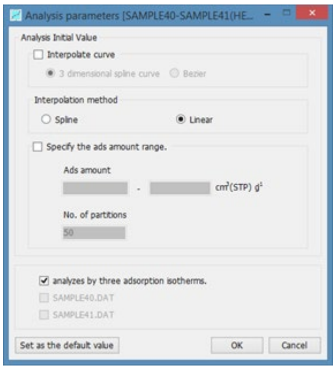
→ Operation P.28 “Open file”

2 When the 1st data is read, select “Read the second data” is displayed as shown in the right figure.

3 Select “File(F)” and then select “Read additional data(A)” from the “Analysis” method menu to read the 2nd data. Or, select “Additional read” from the right click menu to read the 2nd data. (Also, data can be read by drag & drop operation.)


Read the second data

- To read the 3rd data, repeat the step 3. Also, selecting [Analysis with three adsorption isotherms] in [Analysis parameters] enables analysis with three isotherms.


Analysis parameters [SAMPLE40-SAMPLE41(HE...

Analysis Initial Value

☐ Interpolate curve

● 3 dimensional spline curve　○ Bezier

Interpolation method

○ Spline　● Linear

☐ Specify the ads amount range.

Ads amount

- cm³(STP) g⁻¹

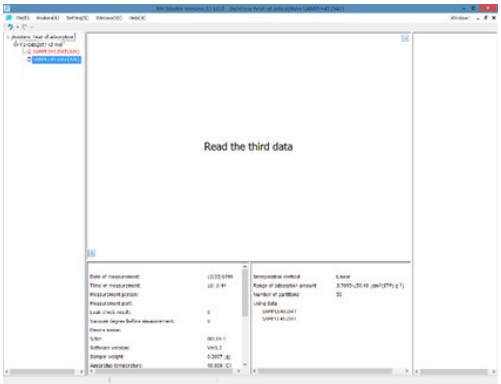
No. of partitions

50

☑ analyzes by three adsorption isotherms.

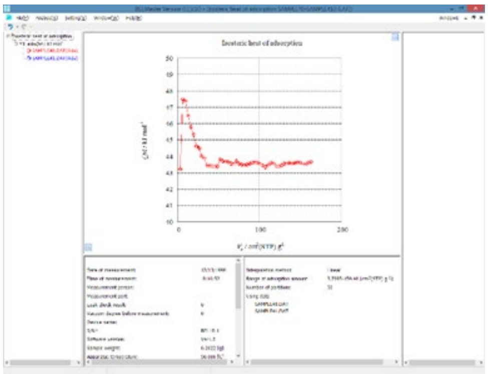
☐ SAMPLE40.DAT

☐ SAMPLE41.DAT


Read the third data

4 Obtain the isosteric heat of adsorption from these two sets of data.

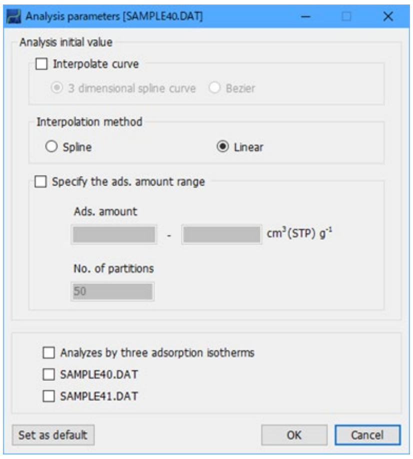
- The right figure shows the result obtained from a measurement of vapor adsorption into non-porous silica (at 25°C and 40°C).



About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu. “Analysis parameters” window shown below will appear. Change the settings as needed.



Analysis parameters [SAMPLE40.DAT]

Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Interpolation method

○ Spline ● Linear

☐ Specify the ads. amount range

Ads. amount ______ - ______ cm^3(STP) g^{-1}

No. of partitions 50

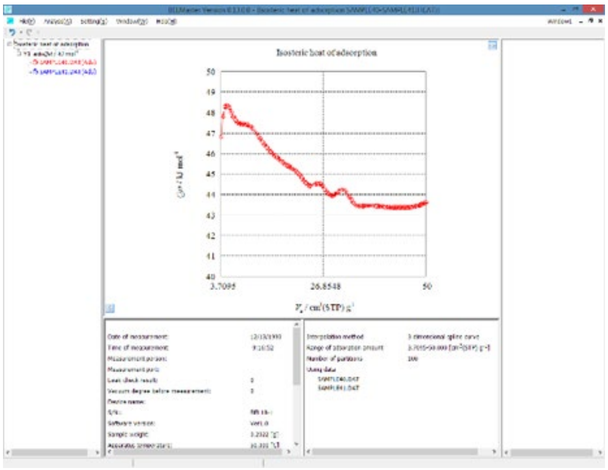
☐ Analyzes by three adsorption isotherms

☐ SAMPLE40.DAT

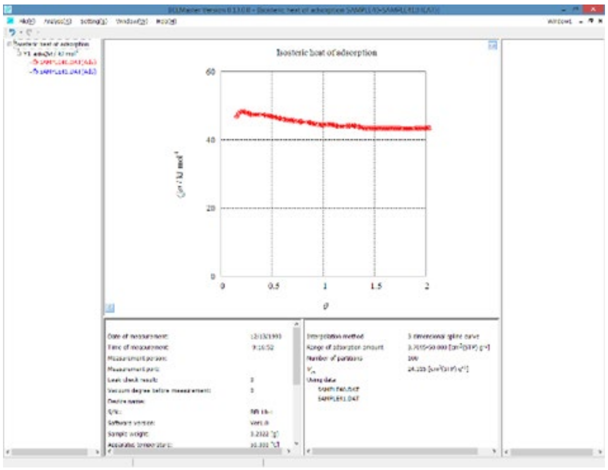
☐ SAMPLE41.DAT

- For details about items not described here, see “Analysis parameters setting”, on P.37.
- When [Specify the ads amount range] is selected, the software will calculate the Isosteric heat of adsorption specified in the table below (“ads amount” and “No.of partitions (5 ≤ “No. of partitions ≤ 500)).
- When [*θ* (surface coverage)] in X-axis display setting is selected, input the range in surface coverage.

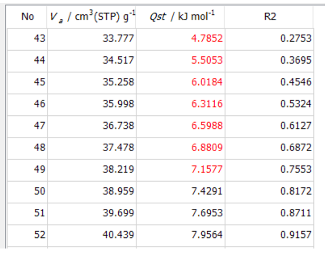
The figure on the right is the result of isosteric heat of adsorption specified ads amount (3.7095 to 50.000 cm^3 (STP) g^{-1}) and No. of partitions (100).



The right graph shows a result of isosterioc heat of adsorption, wherein surface coverage is plotted on the X-axis.



When performing an analysis using adsorption isotherm data for each temperature of $T_1 < T_2 < T_3$, if the pressure value at a certain adsorption amount is not $P_1 < P_2 < P_3$, the heat of adsorption is displayed in red text in the display numerical data and report output file.



No	V_a / cm^3(STP) g^{-1}	Qst / kJ mol^{-1}	R2
43	33.777	4.7852	0.2753
44	34.517	5.5053	0.3695
45	35.258	6.0184	0.4546
46	35.998	6.3116	0.5324
47	36.738	6.5988	0.6127
48	37.478	6.8809	0.6872
49	38.219	7.1577	0.7553
50	38.959	7.4291	0.8172
51	39.699	7.6953	0.8711
52	40.439	7.9564	0.9157

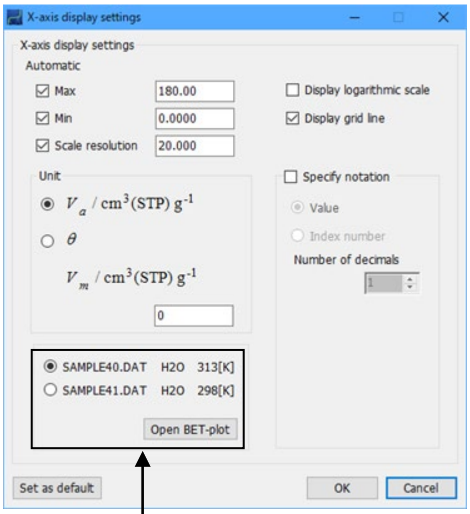
Display numerical data

➢ X axis display settings

For analysis of isosterioc heat of adsorption, “V_a / cm^3 (STP) g^{-1} or “θ” can be selected for the X-axis unit in “Settings(S)” – “X-axis display settings(X)”.

- V_a / cm3(STP) g^{-1}　　Indicates adsorption amount.
- θ　　Indicates surface coverage.

- Enter monomolecular adsorption amount V_m / cm^3 (STP) g^{-1}.
- Monomolecular adsorption amount can be obtained by BET plot.


X-axis display settings

X-axis display settings

Automatic

☑ Max 180.00

☑ Min 0.0000

☑ Scale resolution 20.000

☐ Display logarithmic scale

☑ Display grid line

Unit

● V_a / cm^3(STP) g^{-1}

○ θ

V_m / cm^3(STP) g^{-1} 0

☐ Specify notation

● Value

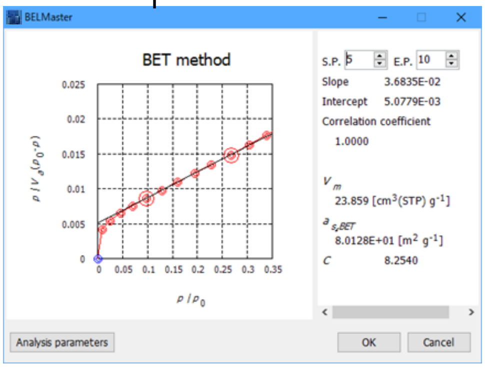
○ Index number

Number of decimals 1

● SAMPLE40.DAT H2O 313[K]

○ SAMPLE41.DAT H2O 298[K]

For calculation of amount of monomolecular layer adsorption, the system executes BET-plot analysis with selected data.
If you push OK button after selecting the point for analysis, the monolayer amount is reflected to X-axis display settings automatically.


BELMaster

S.P. 5 E.P. 10

Slope 3.6835E-02

Intercept 5.0779E-03

Correlation coefficient 1.0000

V_m 23.859 [cm^3(STP) g^{-1}]

$a_{s,BET}$ 8.0128E+01 [m^2 g^{-1}]

C 8.2540

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired setting of Y axis.

Fractal dimension

Description

Generally, it is known that actual surfaces are heterogeneous, including nonporous sample. Therefore, it can be considered that actual adsorption phenomenon is not applied to simple two-dimensional surface.
In consideration of the above, the theory of fractal dimension is an extremely effective means to indicate a degree of surface heterogeneous.

Fractal geometry was proposed by Mandelbrot 1), and applied to adsorbing phenomenon by Pfeifer and Avnir 2).
Assuming that a number of adsorbed molecules is N_{m} when adsorbate with adsorption area σ comprises a monomolecular layer, N_{m} is determined by the following equation 3).

$$N_{\mathrm{m}} = C\,\sigma^{-\frac{D}{2}} \tag{1}$$

Wherein, C is a constant, and D indicates fractal dimension. When $D = 2$, or when the surface is completely homogeneous, C is almost equal to the surface area. Equation (1) expresses that minute surface heterogeneous cannot be detected if the adsorbate molecule is large, but If the adsorbate molecule is small, surface heterogeneous can be detected, so that the number of adsorption molecules increases.
As described above, in most cases, actual surfaces have heterogeneous even with nonporous sample. Therefore, fractal dimension D is generally a value (with self-similarity) between 2 (flat surface) and 3 (three-dimensional structure).

Pfeiffer et al. and Gennes expressed adsorption isotherm on fractal surface by developing FHH (Frankel – Halsey – Hill) equation.

$$\ln\left(\frac{p}{p_0}\right) = -\,\frac{\alpha}{k_{\mathrm{B}}\,T\,{V_{\mathrm{a}}}^{n}} \tag{2}$$

Wherein, α is a coefficient depending on interaction between adsorbent and adsorbate, and between adsorbates, k_{B} is Boltzmann constant, and V_{a} is amount of adsorption.
With fractal dimension D, n is expressed by the following equation.

$$n = \frac{3}{3-D} \tag{3}$$

By transforming Equation (2), correlation between relative pressure and amount of adsorption is expressed as a straight line.

$$\ln V_{\mathrm{a}} = -\,\frac{1}{n}\,\ln\left(\ln\left(\frac{P_0}{P}\right)\right) + \ln\left(\frac{\alpha}{k_{\mathrm{B}}\,T}\right) \tag{4}$$

For fractal dimension analysis, it is also proposed that adsorbate surface tension should be considered.
(For the FHH equation given in Equation (2), adsorbate surface tension is not considered.)

When surface tension is not considered, fractal dimension D is obtained from Equation (3) as follows:

$$D = 3\left(1 - \frac{1}{n}\right) \tag{5}$$

When surface tension is considered, fractal dimension D is obtained by the following equation.

$$D = 3 - \frac{1}{n} \tag{6}$$

If slope of Equation (4) is obtained from Equations (5) and (6), fractal dimension D can be determined.

≪Reference≫

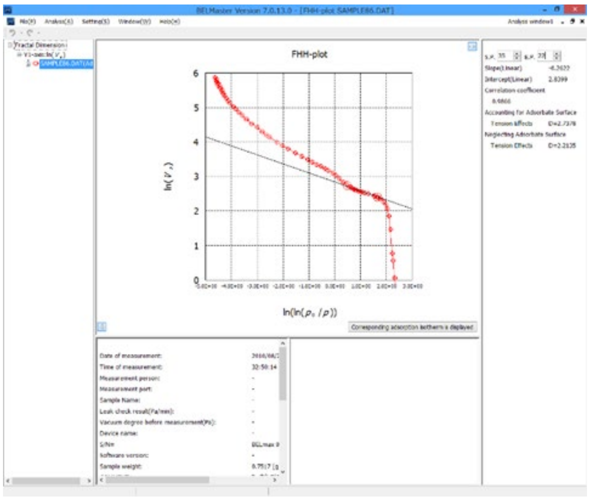
- B. Mandelbrot, The Fractal Geometry of Nature, W. H. Freeman and Company (1982).
- P. Pfeifer and D. Avnir, “Chemistry in noninteger dimensions between two and three. I. Fractal theory of heterogeneous surfaces”, J. Chem Phys., 79, 3558 (1983).
- D. Farin and D. Avnir, Fractal Approach to Heterogeneous Chemistry of Silica, John Wiley (1989).

Operation

Operation of analysis software and analysis result

1 Select “Analysis(A)” and then “Fractal dimension” from the analysis window menu.

→ Operation P.28 “Open file”



2 A fractal dimension analysis graph is displayed as shown on the right, where an approximation straight line is automatically drawn.

3 Select start point and end point of the approximation straight line in a range subject to multimolecular layer adsorption.

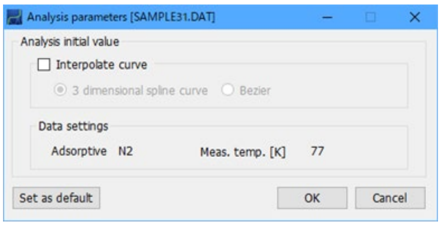
4 Based on slope of the approximation straight line, both the fractal dimension in consideration of surface tension and the fractal dimension without consideration of surface tension are displayed. Correlation coefficient of this approximation straight line is also displayed.

Analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu. “Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37.



Analysis parameters [SAMPLE31.DAT]

Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Data settings

Adsorptive N2 Meas. temp. [K] 77

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

➢ Y axis display settings

Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

Difference of adsorption isotherm

Description

The diffirence between two isotherms can be obtained with this analysis.

This is a useful method for analysis of chemisorption amount.

Operation

Operation of analysis software

1 Select “Analysis(A)” and then “Difference of adsorption isotherm” from the analysis window menu.

- This analysis reads two isotherms.

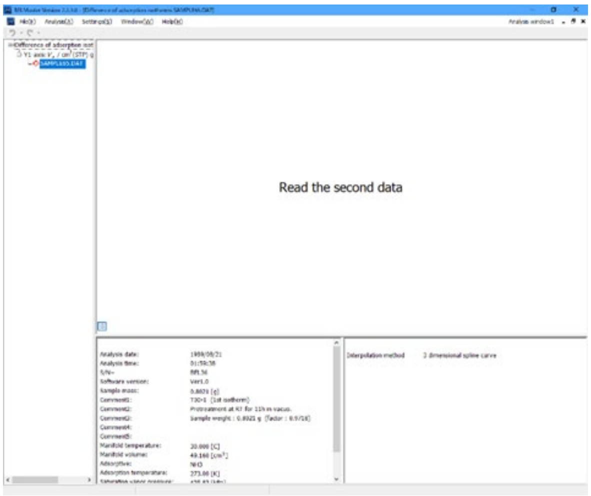
→ Operation P.28 “Open file”

2 When the 1st data is read, “Read the second data” is displayed as shown in the right figure.

3 From the analysis window menu, select “File(F)” → “Overlay(O)” to read the 2nd data.

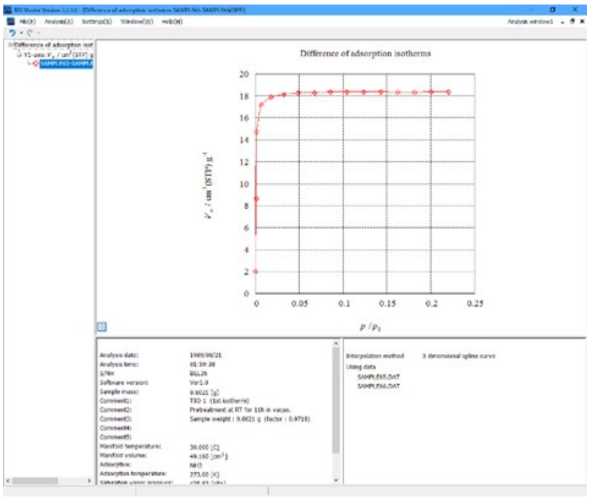
Or, select “Overlay(O)” from the right click menu to read the 2nd data.

(Also, data can be read by drag & drop operation.)

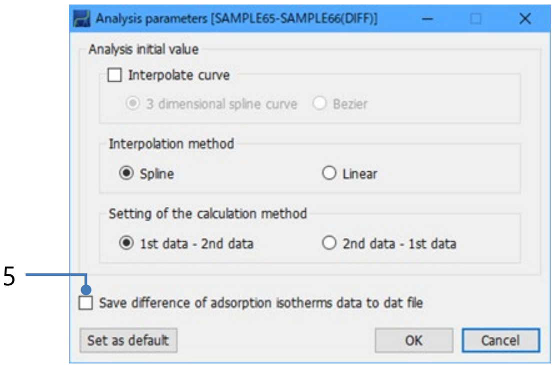


4 Obtain the difference of adsorption isotherm from these two sets of data. The chemical adsorption of ammonia by titanium oxide can be calculated as 18.4 cm^3(STP) g^{-1}.

- The software 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.



5 The data obtained from a “difference of adsorption isotherms” can be saved in an “adsorption isotherm” file. To save a difference of adsorption isotherm, select “Settings(S)"→ “Analysis parameters settings(A)” from the analysis window menu, and select “Save difference of adsorption isotherms data to dat file”. Click OK button.



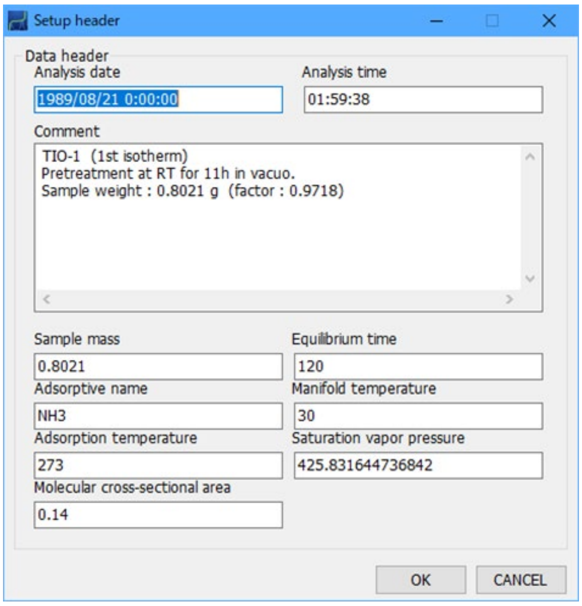
Analysis initial value
☐ Interpolate curve
○ 3 dimensional spline curve ○ Bezier

Interpolation method
● Spline ○ Linear

Setting of the calculation method
● 1st data - 2nd data ○ 2nd data - 1st data

☐ Save difference of adsorption isotherms data to dat file

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.



Data header

Analysis date: 1989/08/21 0:00:00

Analysis time: 01:59:38

Comment:
TIO-1 (1st isotherm)
Pretreatment at RT for 11h in vacuo.
Sample weight : 0.8021 g (factor : 0.9718)

Sample mass: 0.8021

Equilibrium time: 120

Adsorptive name: NH3

Manifold temperature: 30

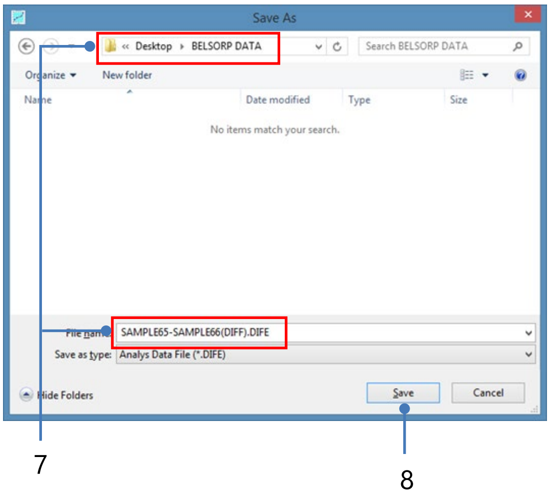
Adsorption temperature: 273

Saturation vapor pressure: 425.831644736842

Molecular cross-sectional area: 0.14

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 software will save the data.



No items match your search.

File name: SAMPLE65-SAMPLE66(DIFF).DIFE

Save as type: Analys Data File (*.DIFE)

9 The data can be analyzed later by selecting “File(F),” “Open,” and then the (analysis name). In the example above, the software analyzes the saved “difference of adsorption isotherm” using a Langmuir analysis, and calculates the volume of ammonia chemisorbed by titanium oxide.

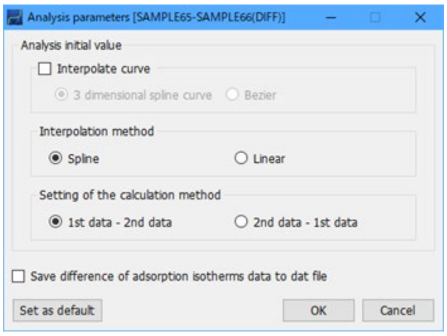
About analysis parameters settings

➢ Analysis parameters settings

Select “Settings(S)” and then “Analysis parameters settings(A)” from the analysis window menu.

“Analysis parameters” window shown below will appear. Change the settings as needed.

- For details about items not described here, see “Analysis parameters setting”, on P.37.



Analysis parameters [SAMPLE65-SAMPLE66(DIFF)]

Analysis initial value

☐ Interpolate curve

◉ 3 dimensional spline curve ○ Bezier

Interpolation method

◉ Spline ○ Linear

Setting of the calculation method

◉ 1st data - 2nd data ○ 2nd data - 1st data

☐ Save difference of adsorption isotherms data to dat file

➢ X axis display settings

Select “Settings(S)” → “X axis display settings(X)” to select desired unit of X axis.

➢ Y axis display settings

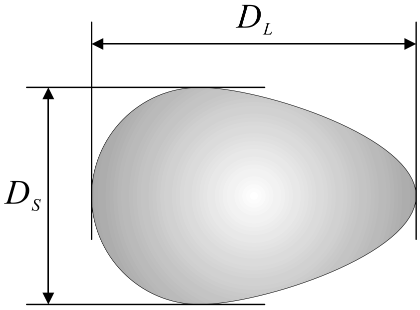
Select “Settings(S)” → “Y axis display settings(Y)” to select desired unit of Y axis.

Molecular probe method

Description

In case of adsorbent with very small pores, it is difficult to calculate pore size distribution 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 chemisorption has to be selected for the probe. The molecular size used varies depending on pore 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-sectional area in case of cyrinder-shaped pore, are used (Refer to the right diagram.).



Operation

1 Using adsorption isotherms from some types of adsorbates with different molecular diameters, calculate the pore volume using a DA or other plot.

Operation of analysis software

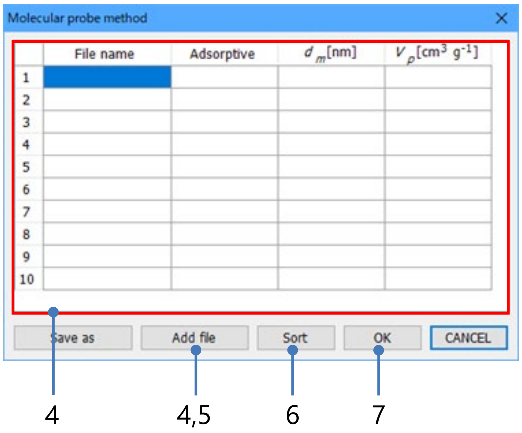
2 Select “Analysis(A)” and then “Molecular probe method” from the analysis window menu.

→ Operation P.28 “Open file”

3 The “Molecular probe method” numerical data window will appear.

4 Enter an “File name”, “Adsorptive name”, “d_m (adsorbate molecular diameter)”, and “V_p (pore volume) ”.

- If molecular probe analysis data is already stored, click Add file and you can select a data. Change the numerical values as needed.

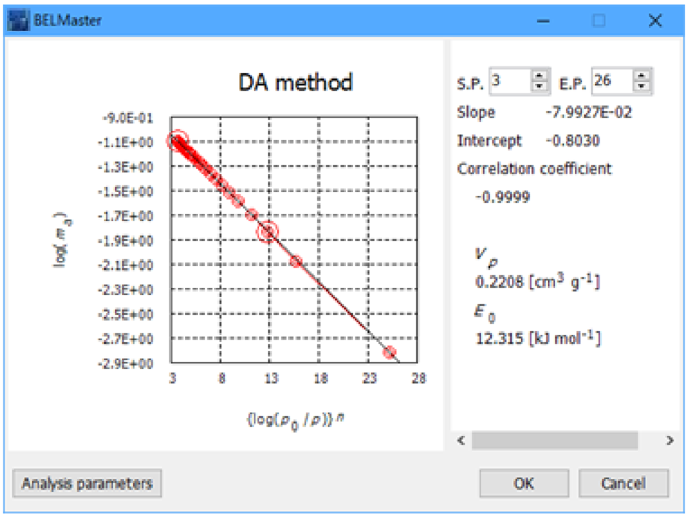


	File name	Adsorptive	d_m[nm]	V_p[cm^3 g^{-1}]
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				

5 If you select a DAT file with the Add file button, the DA plot analysis window automatically opens.

→ P. 169 ”DA plot”

Specify a range to draw a straight line, and click on the OK button. Then, the analysis result will be reflected in the “Molecular probe method” numerical data window.



S.P. 3 E.P. 26

Slope -7.9927E-02

Intercept -0.8030

Correlation coefficient -0.9999

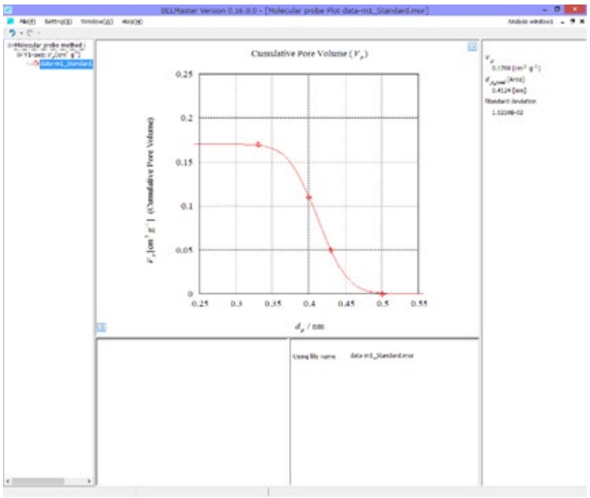
V_p 0.2208 [cm^3 g^{-1}]

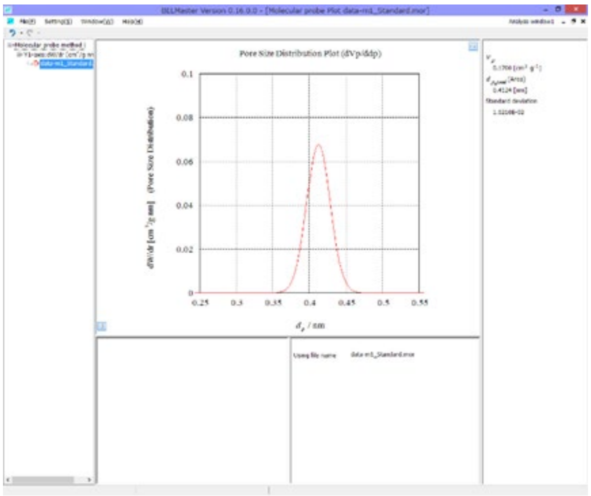
E_0 12.315 [kJ mol^{-1}]

6 Click on the Sort button, the software will sort data in order of larger to smaller d_m (adsorbate molecular diameter).

- Click on the Save as or OK button and the software will sort the data automatically.

7 After entering data, click on the OK button and the window will display the "Cumulative Pore Volume" (lower left figure) or "Pore Size Distribution Plot" (lower right figure). The "Cumulative Pore Volume" is a graph drawn by plotting pore volume (V_p / cm^3 g^{-1}) based on pore diameter (d_p / nm) using the data entered in 4. The "Pore Size Distribution Plot" is a graph differentiating the "Cumulative Pore Volume".



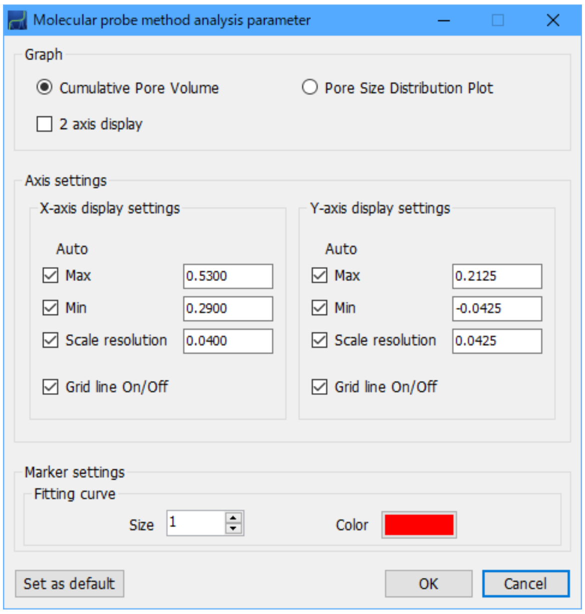


About editing data

1 Select "Settings(S)" and "Analysis parameter settings(A)" on the analysis window menu.

2 The window will show the "Molecular probe method

Analysis parameter" window. You can select graph type (you can also display the both graph on a window) specify X and Y axis, and colors.


Molecular probe method analysis parameter

Graph
● Cumulative Pore Volume ○ Pore Size Distribution Plot
☐ 2 axis display

Axis settings

X-axis display settings
Auto
☑ Max 0.5300
☑ Min 0.2900
☑ Scale resolution 0.0400
☑ Grid line On/Off

Y-axis display settings
Auto
☑ Max 0.2125
☑ Min -0.0425
☑ Scale resolution 0.0425
☑ Grid line On/Off

Marker settings
Fitting curve
Size 1
Color 🟥

NLDFT/GCMC method

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, cylindrical or 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.

$$\Omega[\rho_{\mathrm{L}}(r)] = F[\rho_{\mathrm{L}}(r)] - \int \rho_{\mathrm{L}}(r)\ [\mu - V_{\mathrm{ext}}(r)]\mathrm{d}r \tag{1}$$

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 $V_{\mathrm{ext}}(r)$ is different depending on pore model. Details are described in the next section.

$$F[\rho_\mathrm{L}(r)] = F_\mathrm{h}[\rho_\mathrm{L}(r);\ d] + \frac{1}{2}\int\int \mathrm{d}r\,\mathrm{d}r'\rho_\mathrm{L}(r)\,\rho_\mathrm{L}(r')\,\phi_\mathrm{att}(|r-r'|) \tag{2}$$

Gravitational force potential ϕ_{att} can be obtained with Weeks-Chandler-Anderson equation5).

$$\phi_\mathrm{att}(|r-r'|) = \phi_\mathrm{ff}(|r-r'|) \quad \text{at} \quad |r-r'| > r_\mathrm{m} \tag{3}$$

$$= -\varepsilon_\mathrm{ff} \quad \text{at} \quad |r-r'| < r_\mathrm{m} \tag{4}$$

$$r_\mathrm{m} = 2^{1/6}\,\sigma_\mathrm{ff} \tag{5}$$

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}).

$$F_\mathrm{h}[\rho_\mathrm{L}(r)] = F_\mathrm{id}[\rho_\mathrm{L}(r)] + F_\mathrm{ex}[\rho_\mathrm{L}(r);d] \tag{6}$$

Wherein, the term of ideal gas (F_id) is expressed by the following equation.

$$F_\mathrm{id}[\rho_\mathrm{L}(r)] = k\,T\int \mathrm{d}r\,\rho_\mathrm{L}(r)\left[\ln\left(\Lambda^3\rho_\mathrm{L}(r)\right)-1\right] \tag{7}$$

$\Lambda = h/(2\,\pi\,m\,k\,T)^{1/2}$ indicates de Broglie wave. m indicates molecular weight of adsorptive, and h and k are Planck's constant and Boltzmann's constant, respectively.

The term of excessive amount F_ex is expressed by the following equation.

$$F_\mathrm{ex}[\rho_\mathrm{L}(r);d] = k\,T\int \mathrm{d}r\,\rho_\mathrm{L}(r)\,f_\mathrm{ex}[\bar{\rho}(r);d] \tag{8}$$

Helmholts free energy per molecule of hard sphere (f_ex) is expressed with the equation below.

$$f_\mathrm{ex}[\bar{\rho}(r);d] = \mu_\mathrm{h}[\bar{\rho};d] - \frac{P_\mathrm{h}[\bar{\rho}(r);d]}{\bar{\rho}(r)} - k\,T\left[\ln\left(\Lambda^3\rho_\mathrm{L}(r)\right)-1\right] \tag{9}$$

In the above equation, μ_h and P_h indicate chemical potential and pressure respectively, which are calculated by Carnahan-Starling equation1, 7).

$$P_\mathrm{hd}[\bar{\rho}] = \bar{\rho}\,k\,T\,\frac{1+X+X^2+X^3}{(1-X)^3} \tag{10}$$

$$\mu_\mathrm{h}[\bar{\rho}] = k\,T\left[\ln(\Lambda^3\bar{\rho}) + \frac{8X-9X^2+3X^3}{(1-X)^3}\right] \tag{11}$$

$$X = \frac{\pi}{6}\,\bar{\rho}\,d^3 \tag{12}$$

In this step, NLDFT uses Tarazona theory of smoothed function to calculate density in adsorption phase1, 2).

$$\bar{\rho}(r) = \int \mathrm{d}r'\,\rho_\mathrm{L}(r')\,w\,[|r-r'|;\bar{\rho}(r)] \tag{13}$$

$$w(r;\ \rho) = w_0(r) + w_1(r)\,\rho + w_2(r)\,\rho^2 \tag{14}$$

$$w_0(r) = \frac{3}{4\,\pi\,d^3}\,\Theta\,(d-r) \tag{15}$$

$$w_1(x) = \frac{6}{\pi}\,(a_0 + a_1\,x + a_2\,x^2) \qquad \text{at} \quad x = \frac{r}{d} \le 1 \tag{16}$$

$$w_1(x) = \frac{6}{\pi}\left\{c\,\mathrm{e}^{-\beta_1(x-1)}\sin[\alpha(x-1)] + \mathrm{e}^{-\beta_2(x-1)}(b_0 + b_1\,x + b_2\,x^2 + b_3\,x^3)\right\} \text{at} \quad x = \frac{r}{d} > 1 \tag{17}$$

$$w_2(r) = \frac{5}{4\,\pi}\left(\frac{6}{\pi}\right)\left[6 - 12\frac{r}{d} + 5\left(\frac{r}{d}\right)^2\right]\Theta\,(d-r) \tag{18}$$

Θ : Heaviside step function

As described above, density profile can be calculated. Then, density that provides minimum grand potential is calculated, and the calculation result is equilibrium state.

$$\frac{\delta\Omega[\rho_{\mathrm{L}}(r)]}{\delta\rho_{\mathrm{L}}(r)} = 0 \quad \text{at} \quad \rho_{\mathrm{L}} = \rho_{\mathrm{L,eq}} \tag{19}$$

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.

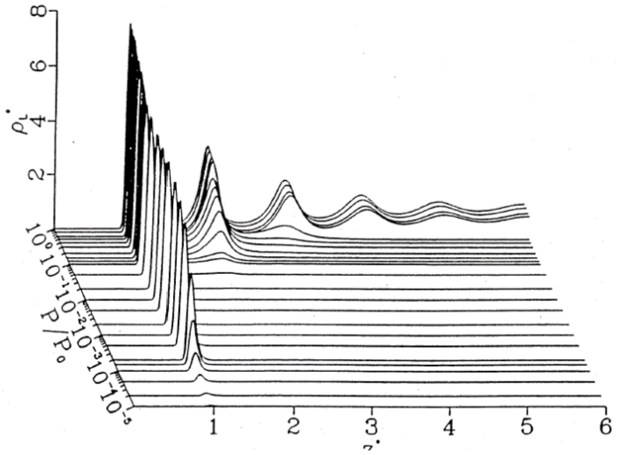


Fig. 1 Localized Density Profile using NLDFT
(p / p_0: Relative pressure, ρ_L^*: Local density,
Z^*: Distance from carbon atom on graphite surface)

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.

➢ 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:

$$N(p) \ = \int_{0}^{\infty} \mathrm{d}H \, f(H) \, \rho(p, H) \tag{20}$$

H : Pore width (nm)

Fluid interaction potential (ϕ_{ff}) can be calculated with the Lennard-Jones 12-6 potential.

$$\phi_{\mathrm{ff}}(r) \ = \ 4 \, \varepsilon_{\mathrm{ff}} \left[\left(\frac{\sigma_{\mathrm{ff}}}{r} \right)^{12} - \left(\frac{\sigma_{\mathrm{ff}}}{r} \right)^{6} \right] \tag{21}$$

Solid–fluid interaction potential (ϕ_{sf}) can be calculated with Steele 10-4-3 potential equation[3)].

$$\phi_{\mathrm{sf}}(z) \ = \ \varepsilon_{\mathrm{w}} \left[\frac{2}{5} \left(\frac{\sigma_{\mathrm{sf}}}{z} \right)^{10} - \left(\frac{\sigma_{\mathrm{sf}}}{z} \right)^{4} - \left(\frac{{\sigma_{\mathrm{sf}}}^{4}}{3\varDelta(z + 0.61\varDelta)^{3}} \right) \right] \tag{22}$$

$$\varepsilon_{\mathrm{w}} \ = \ 2 \, \pi \, \varepsilon_{\mathrm{sf}} \, \rho_{\mathrm{s}} \, {\sigma_{\mathrm{sf}}}^{2} \, \varDelta \tag{23}$$

$$V_{\mathrm{ext}}(z) \ = \ \phi_{\mathrm{sf}}(z) \ + \ \phi_{\mathrm{sf}}(H \ - \ z) \tag{24}$$

➢ Cylindrical pore model

Pores of regular mesoporous material (MCM41, FSM-16 and SBA-15), and zeolite with one-dimensional structure are assumed to be cylindrical shape.

An adsorption isotherm for cylindrical pores is expressed with the equation below:

$$N(p) \ = \ 2 \, \pi \int_{R_{\mathrm{min}}}^{R_{\mathrm{MAX}}} \mathrm{d}R \ f(R) \, \rho(p, R) \, R \tag{25}$$

R : Pore radius (nm)

Fluid interaction potential (ϕ_{ff}) is calculated with Lennard-Jones 12-6 potential Equation (21).

Solid–fluid interaction (ϕ_{sf}) for cylindrical pore model can be calculated with the equation below[10)].

$$\begin{aligned} &\phi_{\mathrm{sf}}(r) \\ &= \varepsilon_{\mathrm{cw}} \left\{ \frac{63}{32} \left[\frac{R - r}{\sigma_{\mathrm{sf}}} \left(1 + \frac{r}{R} \right) \right]^{-10} \times F \left[-\frac{9}{2}, -\frac{9}{2}; 1; \left(\frac{r}{R} \right)^{2} \right] \right. \\ &\left. - 3 \left[\frac{R - r}{\sigma_{\mathrm{sf}}} \left(1 + \frac{r}{R} \right) \right]^{-4} \times F \left[-\frac{3}{2}, -\frac{3}{2}; 1; \left(\frac{r}{R} \right)^{2} \right] \right\} \end{aligned} \tag{26}$$

F (α, β; χ; σ) is a generalized geometrical function, and r is a radial coordinate relative to the center of pore.

$$\varepsilon_{\mathrm{cw}} \ = \ \pi^{2} \, \varepsilon_{\mathrm{sf}} \, \rho_{\mathrm{s}} \, {\sigma_{\mathrm{sf}}}^{2} \tag{27}$$

$$V_{\mathrm{ext}}(r) \ = \ \phi_{\mathrm{sf}}(r) \ + \ \phi_{\mathrm{sf}}(R \ - \ r) \tag{28}$$

➢ 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.

This analysis 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_b 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_{ff} / k_b (K)	σ_{ff} (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_b is 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)]

Gas-Solid	slit pore		Surface molecule number N_s (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.

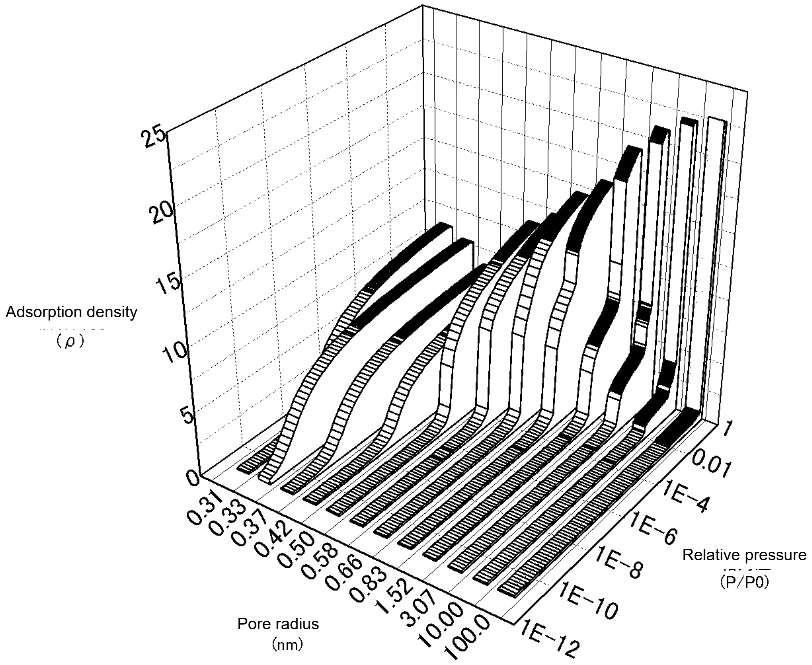


Fig. 2 Theoretical Density Adsorption Isotherm
(Parameters: Cylindrical pore, Adsorptive molecule: Ar, Pore surface atom: O)

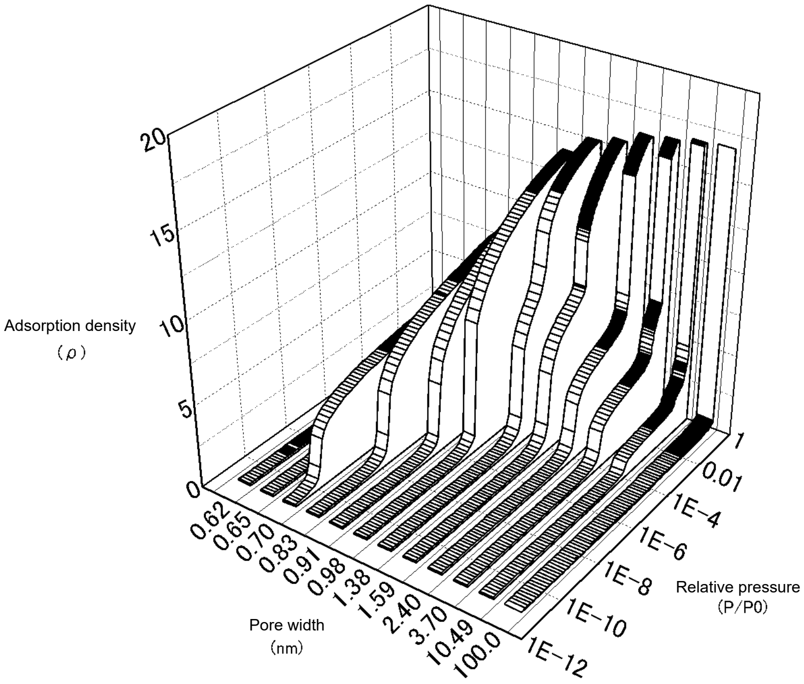


Fig. 3 Theoretical Density Adsorption Isotherm
(Parameters: Slit-shaped pore, Adsorptive molecule: N_2, Pore surface atom: C)

In Fig. 2 and Fig. 3, condensation pressure increases, as the pore diameter becomes large. These figures 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 molecules 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

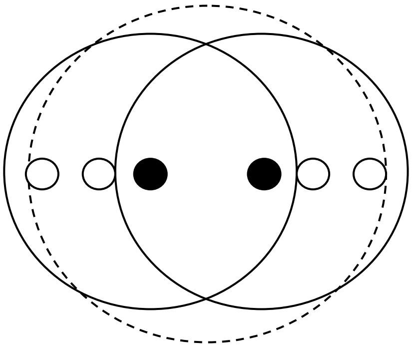


Fig 4 Modeled N_2 molecule, ---- hard sphere system of DFT, — for GCMC (●:LJ center lx, O:charge center lq)

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.

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)	l_x (nm)	l_q (nm)	q (e)
N_2	101.5	0.3615	-	-	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

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)
N_2 / Oxygen[7)]	147.3	0.317	213.8
CO_2 / Carbon	C: 25.0 O: 42.2	C: 0.308 O: 0.321	C: 22 O: 22

5) Integral adsorption isotherm and pore distribution

In equations (20), (25), *N* (*p*) is an integral adsorption isotherm for slit-shaped pore model, and that for cylindrical pore model, respectively. *ρ* (*p*, *H*) and *ρ* (*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.

$$N(p) = \int_0^{\infty} \mathrm{d}H \, f(H) \, \rho(p, H) \tag{20}$$

$$N(p) = 2\pi \int_{R_{min}}^{R_{MAX}} dR \; f(R) \, \rho(p, R) \, R \tag{25}$$

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.

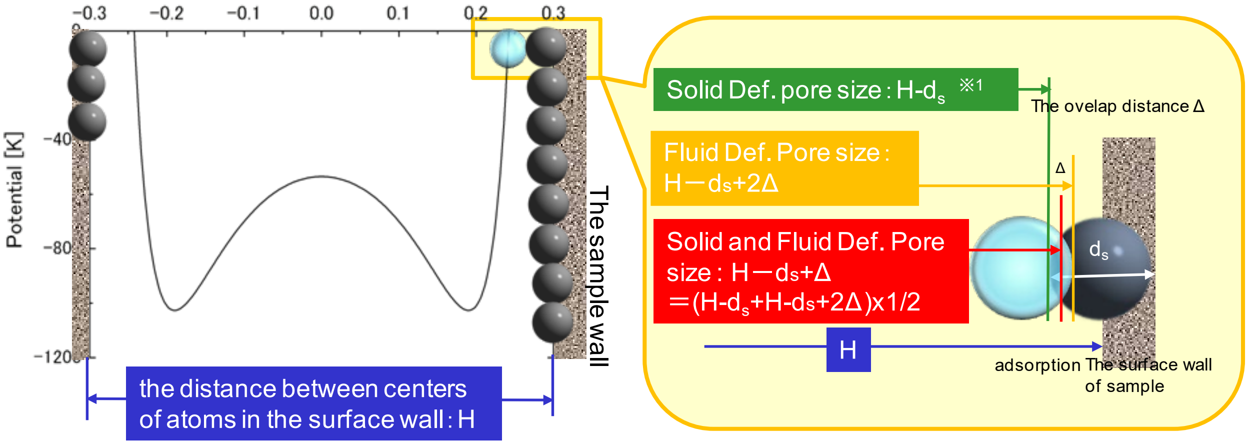
6) Definition of pore diameter

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 : Solid and Fluid Def. Pore Size: Assuming that actual molecule is not a solid sphere, the pore size is defined as the “middle between pore size definitions ① and ②”. We recommend this pore size definition.



≪Reference≫

1) Tarazona, P., *Physical Review* **31**, 2672 (1985);
2) Tarazona, P., Marconi, U.M.B., Evans, R., *Mol Phys*. **52** 847 (1984).
3) Seaton, N.A., Walton, J.R.B., Quirke, N., *Carbon* **27**, 853 (1989).
4) Latoskie, C., Gubbins, K., Quirke, N., *J. Phys. Chem.* **97**, 4786 (1993).
5) Latoskie, C., Gubbins, K., Quirke, N., *Langmuir* **9**, 2693 (1993).
6) Olivier, J.P., *J. Porous Mat.* **2**, 9 (1995).
7) Ravikovitch, P., Vishnyakov, A., Neimark, A.V., *Phys. Rev.* **64**, 011602-1 (2001).
8) Neimark, A.V., *Langmuir* **11**, 4183 (1995).
9) Sweatman, M. B., Quirke, N., *J. Phys. Chem.*, **105**, 1403 (2001).
10) Ravikovitch, P.I., Vishnyakov, A., Russo, R., Neimark, A.V., *Langmuir* **16**, 2311 (2000).
11) 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)
13) S. Hiraide, K. Yamamoto, H. Tanaka, K. Nakai, S. Watanabe, M. T. Miyahara, *Adsorption* **29**, 387 (2023)

Operation

Operation of analysis software

1 Select “Analysis(A)” and then “NLDFT/GCMC” from the analysis window menu.

→ Operation P.28 “Open file”

2 Select a data, the “Analysis parameters” window appears as shown right.

3 Specify the analysis parameters as shown on the right.

- Analysis conditions:

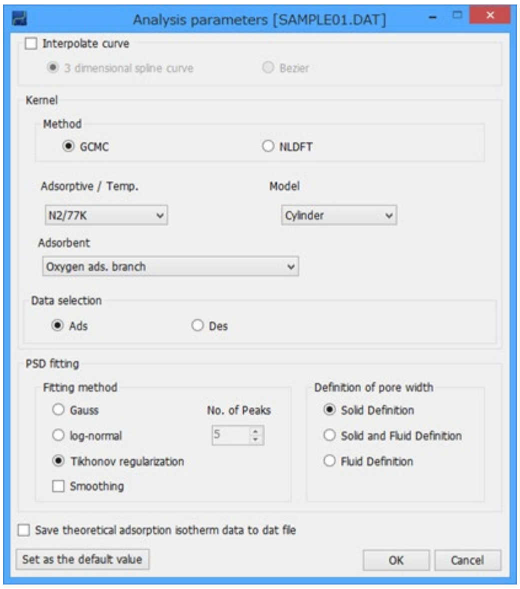
  Adsorptive/Temp.: N_2/77K

  Model: Cylinder

  Adsorbent: Oxygen ads. branch

  Fitting method: Tikhonov regularization

  Definition of pore width: Solid Definition



Analysis parameters [SAMPLE01.DAT]

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

Kernel

Method

● GCMC ○ NLDFT

Adsorptive / Temp.: N2/77K

Model: Cylinder

Adsorbent: Oxygen ads. branch

Data selection

● Ads ○ Des

PSD fitting

Fitting method

○ Gauss

○ log-normal

● Tikhonov regularization

☐ Smoothing

No. of Peaks: 5

Definition of pore width

● Solid Definition

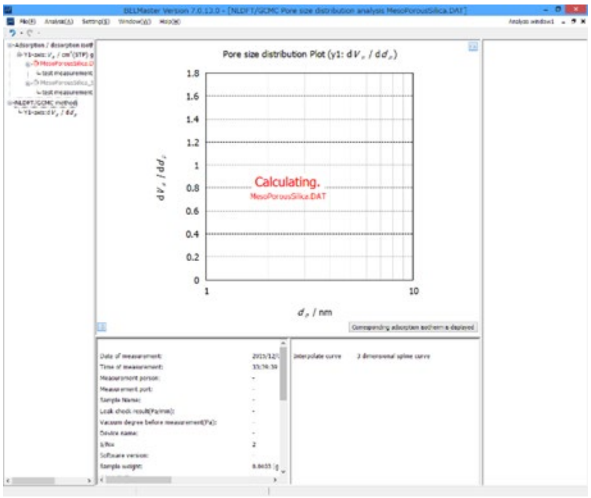
○ Solid and Fluid Definition

○ Fluid Definition

☐ Save theoretical adsorption isotherm data to dat file

4 Press the OK button to start calculation.

5 During calculation, a “Calculating” message is displayed, as shown on the right.

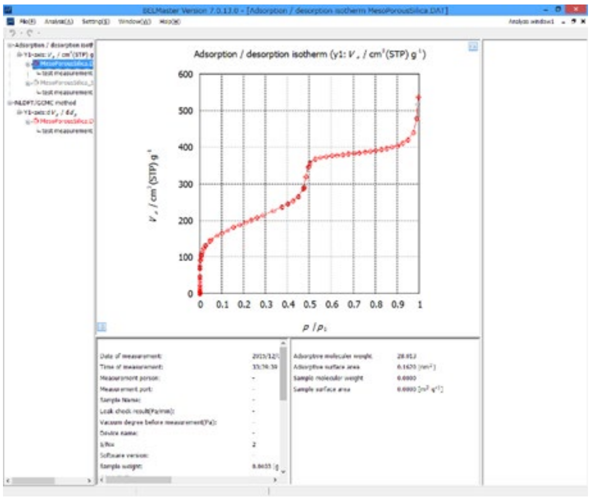


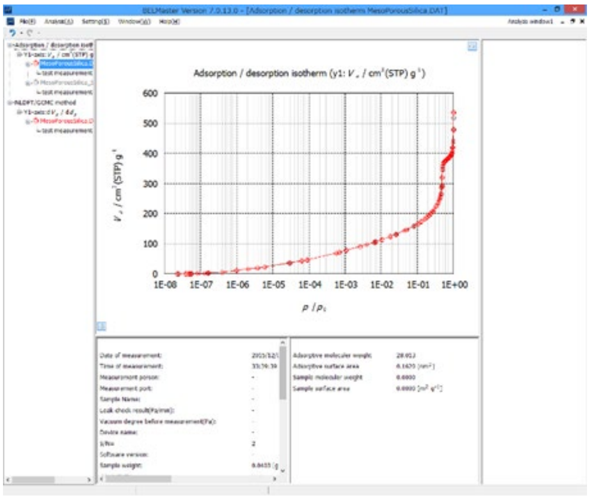
6 After completion of calculation, pore distribution curve, ideal adsorption isotherm and measurement data on the adsorption isotherm are overlaid. The name of ideal adsorption isotherm data file is indicated by the format of “original file name_O_Sim.DAT”. A part of analysis condition settings is displayed in ○.

7 Set the X axis to the “log” scale in “X-axis display settings”.

→ Setting method P.40 ”X-axis display settings”

- The figure below shows an adsorption isotherm, which is obtained by actual measurement of N_2 adsorption in mesoporous silica.

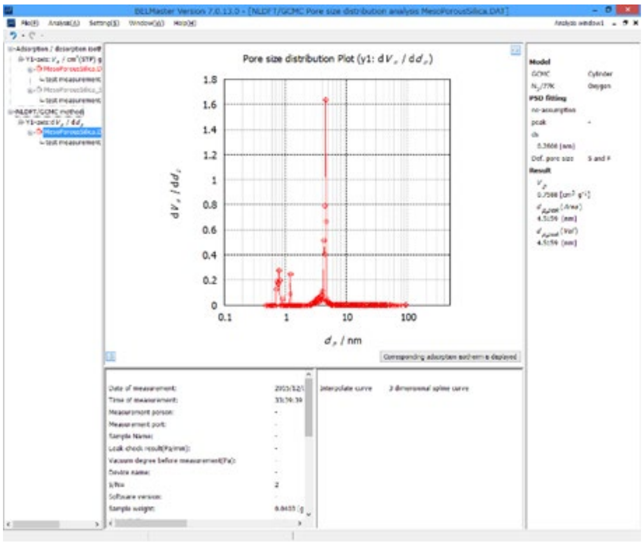




Logarithm

8 The figure on the right shows a pore distribution curve for GCMC analysis. A peak of pore diameter is determined as 4.5 nm as (GCMC analysis result).

For PSD acquisition through NLDFT or GCMC analysis, highly-reliable data can be obtained when an assumed pore shape (cylinder or slit) and chemical composition of pore surface are matched with those of actual measurement data.



About analysis parameters settings

➢ Kernel

- Method

  Select a type of analysis (CGMC or NLDFT).

  A model applicable to analysis varies depending on the selected type of analysis.

- **Adsorptive / Temp.**

  Select a combination of adsorbate and adsorption temperature same as those of the data subject to analysis.

- **Model**

  Select a pore shape of the sample subject to analysis.

  Three types of pore shapes are selectable (Slit / Cylinder / Cage), but some of them may not be selectable depending on the selection of "Method" or "Adsorptive / Temp".

- **Adsorbent**

  Select a model (kernel) used for analysis. Select a model according to the solid surface condition of the sample.

- **Data selection**

  Select an adsorption or desorption branch used for analysis.

  An analysis using a desorption branch is suitable with a model expressed "equilibrium branch is possible".

➢ PSD fitting parameter

- **Fitting method**

  Specify a distribution function that defines pore distribution. In Tikhonov regularization, the fitting is done as the deviation from experimental data is the least.

- **No, of peak**

  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

① Solid Definition :

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 Definition :

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 Definition :

Solid and Fluid Definition: 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.

➢ Save theroritical adsorption isotherm data to dat file

The simulation data is outputted and saved in the folder which the analysis data is saved.

		Slit			Cylinder			Cage		
NLDFT/QSDFT	N2 77 K	Metal Oxide	Carbon Graphitic Carbon	Carbon Roughness Carbon	Metal Oxide	Graphitic Carbon	-	Metal Oxide	Graphitic Carbon	-
		-	○ equilibrium branch is possible 0.39 ~ 75 nm activated carbon etc.	○ equilibrium branch is possible 0.35 ~ 190 nm activated carbon etc.	○ 0.38 ~ 500 nm zeolite etc.	○ 0.84 ~ 600 nm carbon nanotube etc.	-	-	-	-
	Ar 87 K	Metal Oxide	Carbon Graphitic Carbon	Carbon Roughness Carbon	Metal Oxide	Carbon Non-graphitic Carbon	Carbon Graphitic Carbon	Metal Oxide	Graphitic Carbon	-
		-	○ equilibrium branch is possible 0.40 ~ 72 nm activated carbon etc.	○ equilibrium branch is possible 0.35 ~ 220 nm activated carbon etc.	○ 0.36 ~ 400 nm zeolite etc.	○ 0.84 ~ 600 nm cabon nanotube etc.	○ 0.84 ~ 600 nm carbon nanotube etc.	-	-	-
	CO2 273 K	Metal Oxide	Graphitic Carbon	-	Metal Oxide	Graphitic Carbon	-	Metal Oxide	Graphitic Carbon	-
		-	○ 0.35 ~ 5 nm activated carbon etc.	-	-	-	-	-	-	-
GCMC	N2 77 K	Metal Oxide	Carbon Graphitic Carbon	Carbon Roughness Carbon [13]	Metal Oxide	Graphitic Carbon	-	Metal Oxide for mesoporous solid	Graphitic Carbon	-
		-	○ equilibrium branch is possible 0.36 ~ 500 nm activated carbon with ultramicropore etc.	○ equilibrium branch is possible 0.36 ~ 200 nm activated carbon etc.	○ 0.42 ~ 100 nm zeolite, alumina mesoporous silica etc.	○ 0.6 ~ 100 nm carbon nanotube etc.	-	○ 0.42 ~ 20 nm mesoporous silica (SBA-16) etc.	-	-
	Ar 87 K	Metal Oxide	Carbon Graphitic Carbon [13]	Carbon Roughness Carbon [13]	Metal Oxide	Graphitic Carbon	-	Metal Oxide for mesoporous solid	Metal Oxide for microporous solid	Graphitic Carbon
		-	○ equilibrium branch is possible 0.36 ~ 300 nm activated carbon with ultramicropore etc.	○ equilibrium branch is possible 0.36 ~ 300 nm activated carbon etc.	○ 0.42 ~ 100 nm mesoporous silica etc.	-	-	○ 0.42 ~ 20 nm mesoporous silica (SBA-16) etc.	○ 0.46 ~ 10 nm zeolite etc.	-
	CO2 298 K	Metal Oxide	Carbon Graphitic Carbon	Carbon with Ultramicropore [*1]	Metal Oxide	Carbon Non-graphitic Carbon	Carbon Graphitic Carbon	Metal Oxide	Graphitic Carbon	-
		-	○ 0.24 ~ 100 nm activated carbon etc.	○ 0.26 ~ 1.5 nm activated carbon etc.	-	○ 0.66 ~ 600 nm carbon nanotube etc.	○ 0.66 ~ 600 nm carbon nanotube etc.	-	-	-

[*1] It is suitable for the analysis for 0.1 MPa (pore width 0.32 to 1.5 nm) or less.

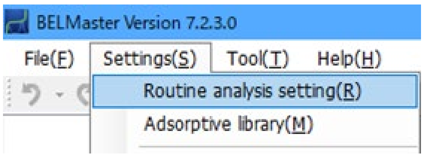
How to use [Routine analysis]

Using this function, you can open selected data with multiple preset analysis methods.

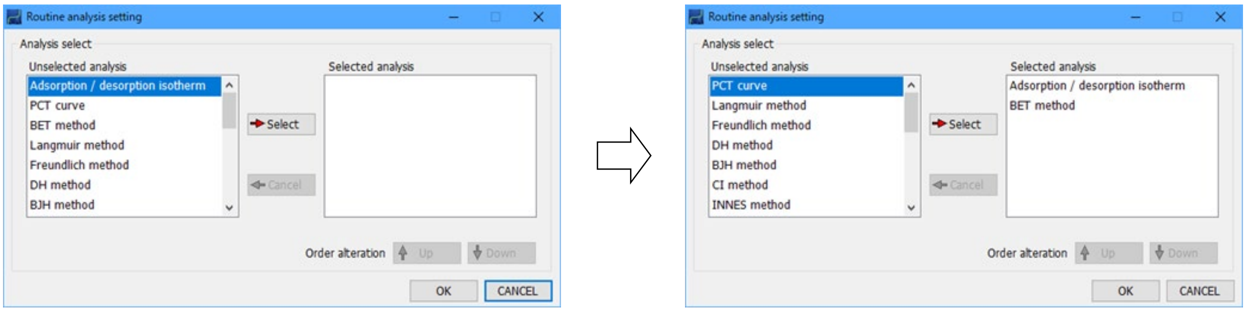
Setting

1 Select “Settings(S)” and then “Routine analysis setting(R)” from the main window menu or the analysis window menu.

2 A “Routine analysis settings” window will appear to allow you to change routine analysis settings.



3 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 analysises. If the analysis in “Selected analysis” is not needed, select the analysis and click on the Cancel button.



4 Click on the OK button to determine the selected analysises.

If you cancel the selected analysises, click on the CANCEL button.

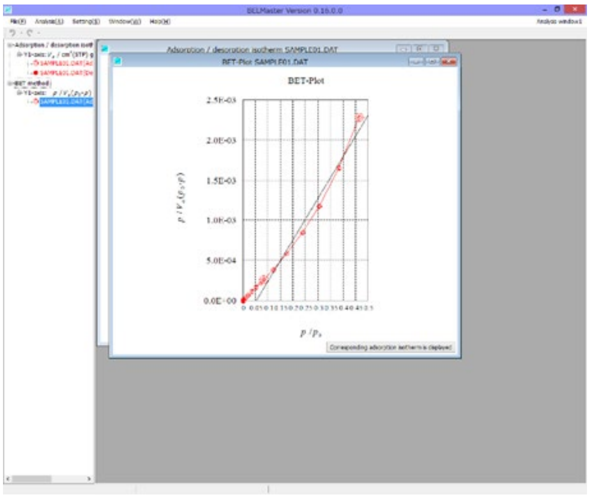
Operation

Operation of analysis software

1 Select “File(F)”, “Open(O)” and then “Routine Analysis” from the main window menu.

2 The file selection window will appear.

3 As shown in the figure on the right, the analyses registered in “Routine analysis settings” will open immediately.



Output an analysis report

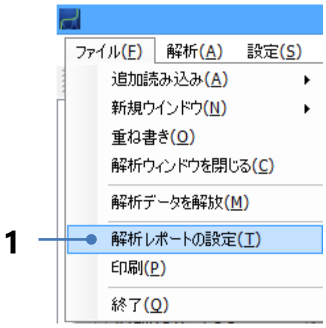
You can output numerical data or graphs as an Excel file (*.XLS), and can be edited with Excel. This function is useful to prepare reports.

- If Microsoft Excel® is not installed, this function cannot be used.

Operation

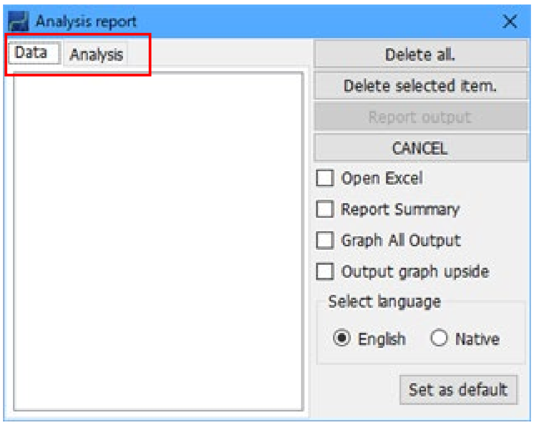
Operation of analysis software

1 Select “File(F)” and then “Report settings(R)” from the analysis window menu.



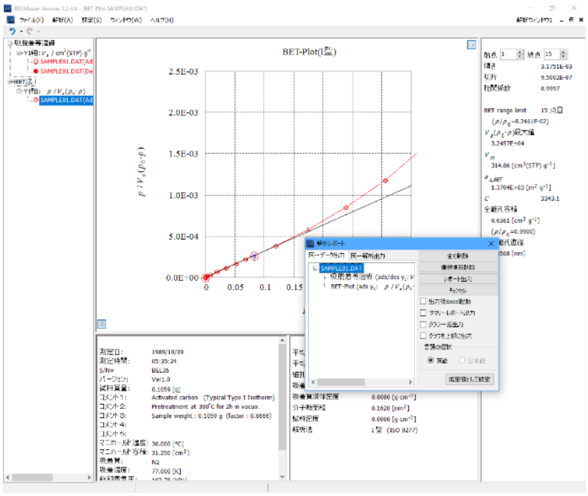
2 The “Analysis report” window appears as shown on the right.

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



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.

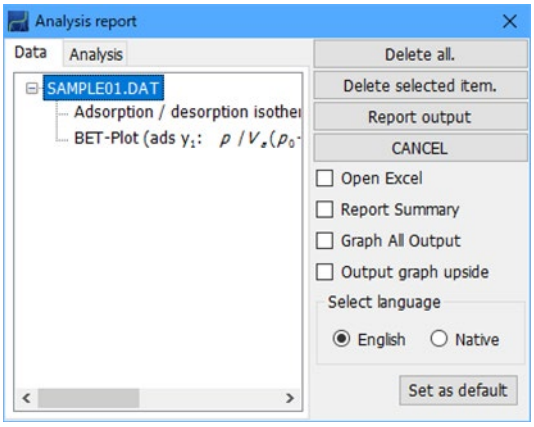


4　After the data is copied, the "Analysis report" window is displayed as shown on the right.

If you check the [Open Excel] checkbox, Excel will automatically open after report output.

If you check the [Report Summary] checkbox, summary report will be prepared.

When the [Data] tab is selected, if you intend to output all graphs at once, check the [Graph All Output] checkbox.

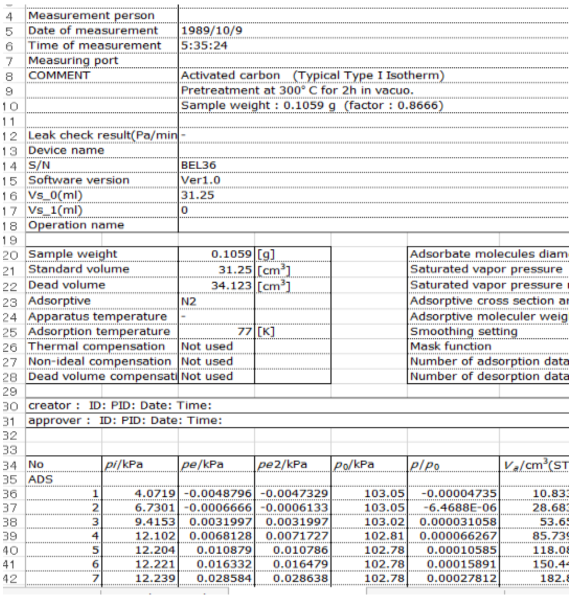


When the [Analysis] tab is selected, if you intend to output an overlay graph, check the [Overlay Graph Output] checkbox.

If you check the [Output graph upside] checkbox, graphs and results for each analysis are output on the upside of each sheet. The information and conditons for measurement are output below them.

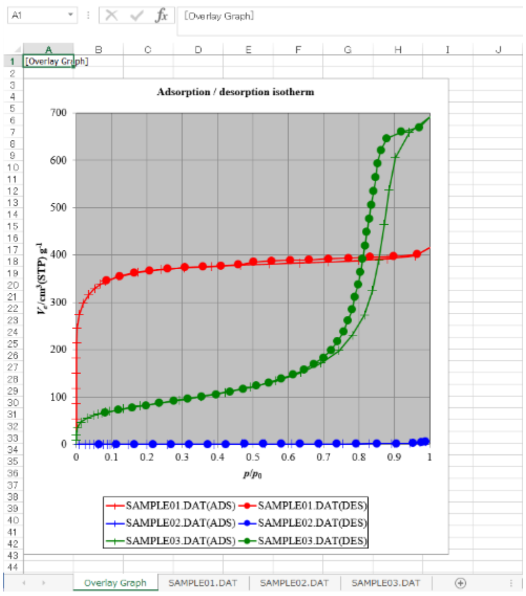
Each item is displayed in a language that has been selected in [Select language].

5　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.



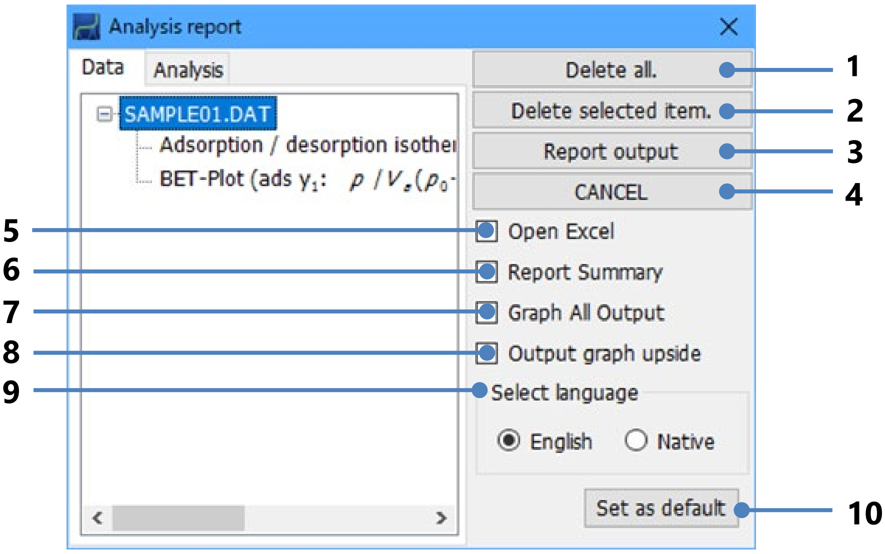
4	Measurement person						
5	Date of measurement		1989/10/9				
6	Time of measurement		5:35:24				
7	Measuring port						
8	COMMENT		Activated carbon (Typical Type I Isotherm)				
9			Pretreatment at 300° C for 2h in vacuo.				
10			Sample weight : 0.1059 g (factor : 0.8666)				
11							
12	Leak check result(Pa/min		-				
13	Device name						
14	S/N		BEL36				
15	Software version		Ver1.0				
16	Vs_0(ml)		31.25				
17	Vs_1(ml)		0				
18	Operation name						
19							
20	Sample weight		0.1059	[g]		Adsorbate molecules diam	
21	Standard volume		31.25	[cm^3]		Saturated vapor pressure	
22	Dead volume		34.123	[cm^3]		Saturated vapor pressure	
23	Adsorptive		N2			Adsorptive cross section ar	
24	Apparatus temperature		-			Adsorptive moleculer weig	
25	Adsorption temperature		77	[K]		Smoothing setting	
26	Thermal compensation		Not used			Mask function	
27	Non-ideal compensation		Not used			Number of adsorption data	
28	Dead volume compensati		Not used			Number of desorption data	
29							
30	creator : ID: PID: Date: Time:						
31	approver : ID: PID: Date: Time:						
32							
33							
34	No	pi/kPa	pe/kPa	$pe2$/kPa	p_0/kPa	p/p_0	V_a/cm^3(ST
35	ADS						
36	1	4.0719	-0.0048796	-0.0047329	103.05	-0.00004735	10.83
37	2	6.7301	-0.0006666	-0.0006133	103.05	-6.4688E-06	28.68
38	3	9.4153	0.0031997	0.0031997	103.02	0.000031058	53.6
39	4	12.102	0.0068128	0.0071727	102.81	0.000066267	85.73
40	5	12.204	0.010879	0.010786	102.78	0.00010585	118.0
41	6	12.221	0.016332	0.016479	102.78	0.00015891	150.4
42	7	12.239	0.028584	0.028638	102.78	0.00027812	182.

Report summary



Overlay Graph

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



1	Deletes copied data.
2	Deletes a selected item only.
3	Outputs an analysis report.
4	Closes the “Analysis report” window.
5	When this checkbox is ON, Excel will open after an analysis report is output.
6	When this checkbox is ON, summary report about analysis output.
7	When this checkbox is ON, graph for all analysis output.
8	When this checkbox is ON, graphs and results for analysis are output on each sheet.
9	Select language which you want to output.
10	Set the present setting as the default value.

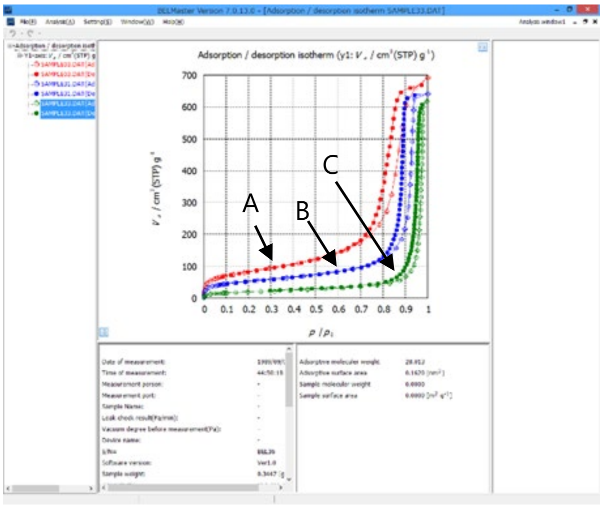
APPENDIX

Sample analysis examples

This chapter shows analysis examples of typical samples.

Silica with mesopores

1 The figure on the right shows nitrogen adsorption isotherms for three types of silica with mesopores (~ macropores).

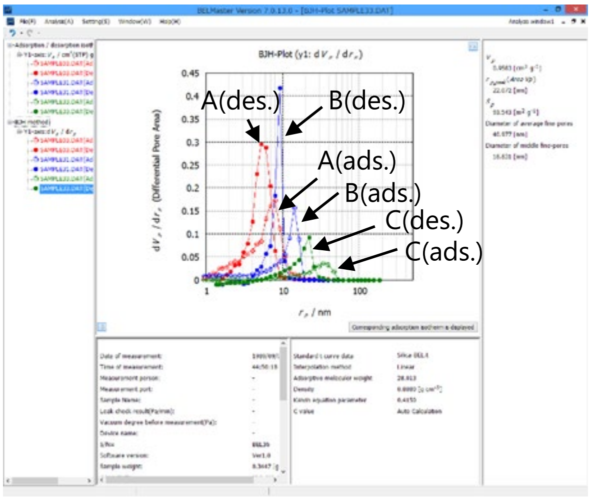


2 These adsorption isotherms display hysteresis (a part that does not match between adsorption process and desorption process), and are type IV adsorption isotherms.

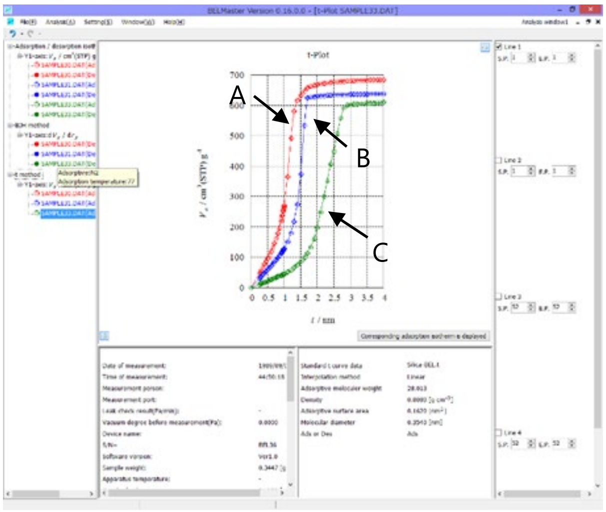
From these conditions, we can determine that these samples have mesopores.

3 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.

4 The figure on the right is a result of the BJH plot compared to the both of adsorption and desorption processes.
The distribution of pores can be obtained from the adsorption process (◎).
The distribution of pores in the neck area (thinner part) can be obtained from the desorption process (○).



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



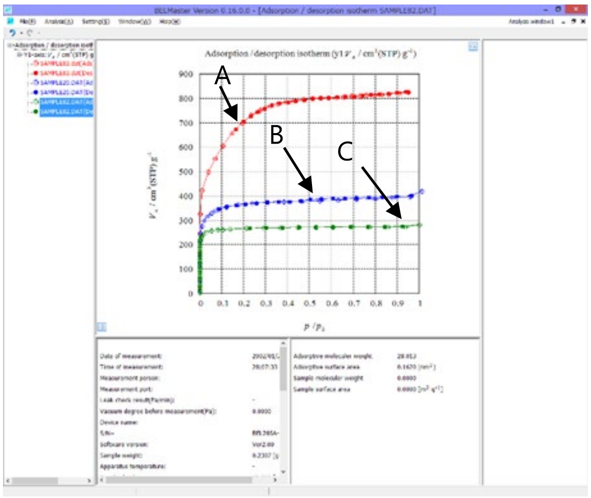
6 Data obtained using the BET plot, BJH plot, and *t*-plot are shown in the table below. We can evaluate sample information (specific area, pore volume etc.) from more than one analysis.

Sample	Silica A	Silica B	Silica C
BET plot	Specific surface area / m^2 g^{-1}		
	302	191	70.0
DH plot	［Adsorption process］ Mesopore radius range (Peak value of distribution)/ nm		
	2 to 15 (8.0)	5 to 18 (14)	up to 55 (34)
	［Adsorption process］ Mesopore volume / cm^3 g^{-1}		
	1.07	0.98	0.95
	［Desorption process］ Mesopore radius range (Distribution peak value) / nm		
	3 to 9 (5.3)	3 to 11 (9.2)	up tp 35 （22)
	［Desorption process］ Mesopore volume / cm^3 g^{-1}		
	1.09	1.00	0.96

Sample	Silica A	Silica B	Silica C
t plot	Specific surface area / m^2 g^{-1}		
	300	189	70.3
	External specific surface area / m^2 g^{-1}		
	6	3	9.8
	Mesopore specific surface area / m^2 g^{-1}		
	294	186	60.5
	Mesopore volume / cm^3 g^{-1}		
	1.03	0.98	0.90

Activated carbon with micropores

1 The figure on the right shows Nitrogen adsorption isotherms for three types of activated carbon with micropores.

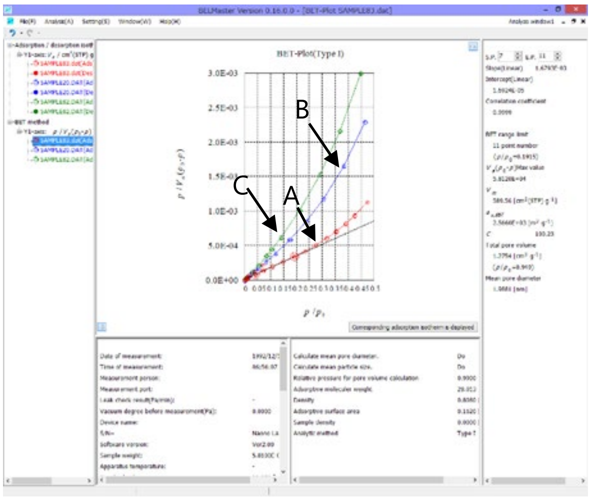


2 These adsorption isotherms have high adsorption volume at a low relative pressure range, and show a type I adsorption isotherm.

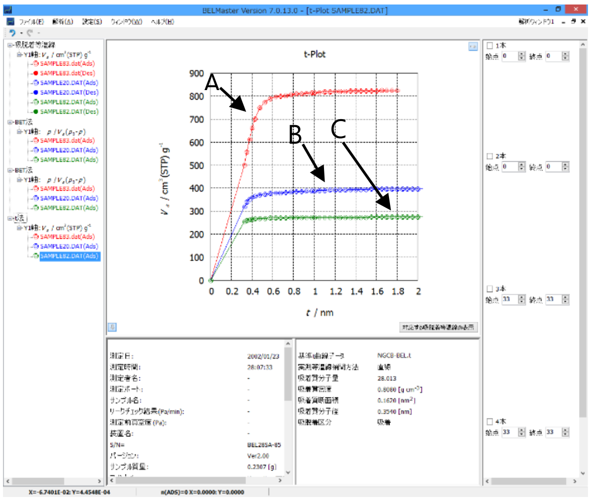
From these conditions, we can determine that these samples have micropores.

3 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.

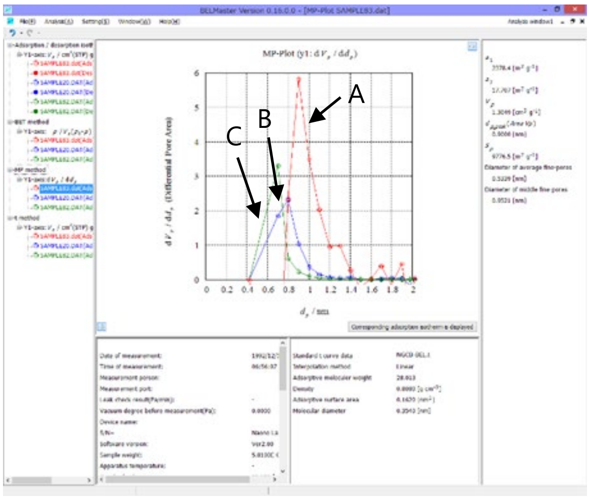
4 The figure on the right is the BET plot from these activated carbons. Activated carbon C has the smallest pore diameter, and the deviation from a straight line is large. When adsorption isotherm is type I (IUPAC classification), select "Type I (ISO 9277)" in "analysis parameter" window. Then calculate the specific area.



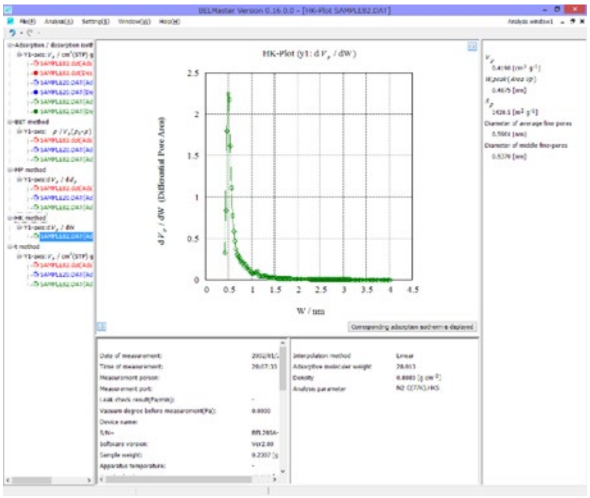
5 The figure on the right is the *t*-plot of these activated carbon samples. It is difficult to obtain the total specific area for activated carbon C. Also, as the pore diameter get smaller, the result may be greatly affected by the micropore effect and the total specific surface value will be larger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



6 The analysis results from an MP plot are shown on the right.



7 The figure on the right is the HK plot of activated carbon C.



8

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 area / m^2 g^{-1}		
	302	191	70.0
	C value (relative pressure range)		
	100 (0.04 ~ 0.19)	2290 (0.00 ~ 0.07)	21700 (1.6E-7 ~ 1.3E-2)
t plot	Total specific surface area / m^2 g^{-1}		
	2550	1500	(1207)
	External specific surface area / m^2 g^{-1}		
	10	8	7
	Micropore specific surface area / m^2 g^{-1}		
	2540	1492	(1200)
	Micropore volume / cm^3 g^{-1}		
	1.26	0.60	0.41
	Pore width, 2*t* / nm		
	0.98	0.80	–
MP plot	Micropore width range (Peak value of distribution) / nm		
	0.7 to 1.5 (0.90)	0.4 to 1.1 (0.80)	0.4 to 0.8 (0.60)
HK plot	Micropore width range (Peak value of distribution) / nm		
	–	–	0.4 to 0.7 (0.49)

About difference of expression for pore size distribution

The pore size distribution is classified into three types; pore volume distribution, pore area distritbution and pore length (depth) distribution.

Now, Consider the cylindrical pore with pore radius (r_p).

Supposing that the length (depth) is L leads the pore volume (V_p) is $\pi\, r_p^2\, L$ and the pore surface area (a_p) is $2\pi\, r_p\, L$. The following equation are obtained by solving the pore size distribution mathematically.

$$\frac{\mathrm{d}V_\mathrm{p}}{\mathrm{dlog}r_\mathrm{p}} = \frac{\mathrm{d}V_\mathrm{p}}{\mathrm{d}r_\mathrm{p}}\,\frac{\mathrm{d}r_\mathrm{p}}{\mathrm{dlog}r_\mathrm{p}} = 2\,\pi\,r_\mathrm{p}\,L\,\times\,r_\mathrm{p} = 2\,\pi\,r_\mathrm{p}{}^2\,L\,[\mathrm{cm^3\,g^{-1}}] \tag{1}$$

$$\frac{\mathrm{d}V_\mathrm{p}}{\mathrm{d}r_\mathrm{p}} = \frac{\mathrm{d}\left(\pi\,r_\mathrm{p}{}^2\,L\right)}{\mathrm{d}r_\mathrm{p}} = 2\,\pi\,r_\mathrm{p}\,L\;\;[\mathrm{cm^3\,g^{-1}\,nm^{-1}}] \tag{2}$$

$$\frac{\mathrm{d}a_\mathrm{p}}{\mathrm{dlog}r_\mathrm{p}} = \frac{\mathrm{d}a_\mathrm{p}}{\mathrm{d}r_\mathrm{p}}\,\frac{\mathrm{d}r_\mathrm{p}}{\mathrm{dlog}r_\mathrm{p}} = 2\,\pi\,L\,\times\,r_\mathrm{p} = 2\,\pi\,r_\mathrm{p}\,L\;\;[\mathrm{m^2\,g^{-1}}] \tag{3}$$

$$\frac{\mathrm{d}a_\mathrm{p}}{\mathrm{d}r_\mathrm{p}} = \frac{\mathrm{d}\left(2\,\pi\,r_\mathrm{p}\,L\right)}{\mathrm{d}r_\mathrm{p}} = 2\,\pi\,L\;\;[\mathrm{m^2\,g^{-1}\,nm^{-1}}] \tag{4}$$

Each expression of pore size distribution shows the following physical definitions from the dimension in Equation (1) ~ (4).

According to the objective for comparison or application, need to select the proper expression for pore size distribution.

Name	Feature
Pore volume distribution	Equation (1) shows pore volume distribution. This distribution has more weight on larger pores. This distribution is suitable for the research of adsorbent and evaluation of adsorption capacity during the adsorption process.
Pore area distribution	Equation (2) and (3) show pore area distribution and the similar form each other. This distribution is suitable for comparing the area of reactive sites on the catalyst during the reaction process.
Pore length distribution	Equation (4) shows pore length distribution. This distribution has more weight on smaller pores. This distribution is suitable for comparing the growth of pore due to activation treatment etc.

Major changes

Major changes from Ver. 6

- On the analysis window, slide window (to show measurement/analysis conditions) and right sub window (to show analysis results) are displayed.
- Display color is specified for each data. Simultaneous display of individual analyses is enabled.
- Supporting zoom-in functions through drag & drop operation
- Supporting Undo and Redo button
- Addition of corresponding adsorption isotherm display function
- Addition of slide display function
- A size of window after activating the software is memorized.
- Display language can be selected (Native or English).
- A header can be added on the print.
- Language for report output and print can be selected (Native or English).
- Length distribution and area distribution ($\mathrm{d}S_\mathrm{p}/\mathrm{d}r_\mathrm{p}$, $\mathrm{d}S_\mathrm{p}/d\mathrm{d}_\mathrm{p}$, $\mathrm{d}S_\mathrm{p}/\mathrm{dlog}r_\mathrm{p}$, $\mathrm{d}S_\mathrm{p}/\mathrm{dlog}d_\mathrm{p}$) can be displayed for pore distribution analysis.
- A point corresponding to measuring relative pressure can be displayed for pore size distribution analysis.
- Average diameter and middle diameter of pores can be calculated.
- Histogram can be displayed.
- A ratio of whole pore volume to the pore volume in the range is calculated.
- Supporting Å display
- Supporting 2 axis display
- Supporting the display of the standard curve using for analysis
- Up to 4 straight lines can be displayed for *t*-plot and α_s-plot.
- For measurement results except for those of nitrogen, *t*-plot, α_s-plot and mesopore analysis are enabled.
- Adsorption and desorption can be simultaneously displayed for *t*, α_s-plot and mesopore analyses.
- Addition of Freundlich analysis
- Addition of CY plot for micropore analysis
- Addition of fractal dimension analysis
- Addition of kernel for GCMC
- Addition of a function to automatically open the DA plot analysis window when a DAT file is selected for the molecular probe method.

Major changes from Ver. 7. 1

- Supporting .NDAT file, recalculation of non-ideality correction and so on is enabled.
- Outputting the graph on upside each sheet for report output is enabled.
- Results of each Y axis are enabled to output at the same time in pore size distribution.
- Names of terms and parameter are comformed the standards (ISO and so on).

Major changes from Ver. 7. 2

- Supporting recalculation with REFPROP
- Addition of standard t, αs-curve
- Addition of kernel for GCMC
- Addition of trial mode
- Addition of MAX G as supported instrument

Major changes from Ver. 7. 3

- Supporting recalculation of the data using AFSM2
- Supporting calculation of average pore diameter using the BET method assuming each pore shape
- Supporting displaying volcano-plot in BET method
- Supporting multiple saved files in “Restart work”
- Addition of batch print function
- Addition of MAX X as supported instrument

Major changes from Ver. 7. 4. 0. 0

- Supporting saving AIF file
- Addition of kernel for GCMC / NLDFT (Ver. 7. 4. 2. 3)

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, CI plot、 INNES plot).

Standard isotherm

Micropore analysis (*t*-plot, α_s plot, and MP plot) and mesopore distribution analysis (DH plot, BJH plot, CI plot and INNES plot) use a standard isotherm for their analysis. In nitrogen adsorption, this analysis software comes with data from 5 nonporous samples (silica, carbon (Graphitized Carbon and non-Graphitized Carbon), alumina, cupper powder), the standard t curves of Harkins-Jura and FHH (Frenken-Halsey-Hill), and 5 standard α_s curves 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.

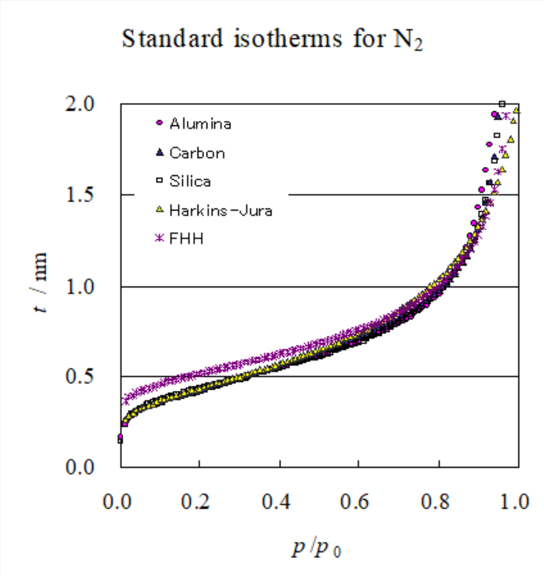


Fig. 1 Standard isotherm using BELMaster

A standard Harkins-Jura t curve can be obtained using the equation below.

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

In addition, the standard FHH isotherm can be calculated using the equation below.

$$t = 0.354 \times \left(\frac{-5.00}{\ln \frac{p}{p_0}} \right)^{\frac{1}{3}} \tag{2}$$

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 low relative pressure range, such as the *t*-plot and MP plot, may cause significant error and we cannot recommend use FHH for these methods.

In the evaluation for carbon black for rubber industry, statistical thickness surface area (STSA) which does not involve the specific surface area in the pore has been used. STSA can be calculated by the following equation.

$$t = 0.088 \times \left(\frac{p}{p_0}\right)^2 + 0.645 \times \left(\frac{p}{p_0}\right) + 0.298 \qquad (3)$$

Analysis by t-plot using Equation (3) in the relative pressure range between 0.2 ~ 0.5 calculate the external specific surface area without the area in the pore whose pore size is 0.86 nm or less.

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:\ MicrotracBEL\BELMaster7\T-Data".

➢ Standard isotherm for *t* plot analysis

The standard isotherm file for a *t* plot has file name extension of ".t".

File name	Adsorbate	Sample
"Silica-BEL.t"	Nitrogen	Silica
"NGCB-BEL.t"		non-Graphitized Carbon
"GCB-BEL.t"		Graphitized Carbon
"Alumina-BEL.t"		Alumina
"CuPowder-BEL.t"		Copper powder
"Harkins-Jura-BEL.t"		-
"FHH-BEL.t"		-
"STSA-BEL.t"		Carbon black
"HydSiO2-Ar_87K-BEL"	Argon	Hydroxylated silica
"DehSiO2-Ar_87K-BEL"		Dehydroxylated silica
"Silica-Kr-BEL.t"	Krypton	Silica

File format: Since the file is encrypted, it cannot be read with commercially-available spreadsheet software.

➢ Standard isotherm for α_s plot analysis

Standard isotherm file for α_s plot: Extension of file name is ".as ".

File name	Sample
"Silica-BEL.as"	Silica
"NGCB-BEL.as"	non-Graphitized Carbon
"GCB-BEL.as"	Graphitized Carbon
"Alumina-BEL.as"	Alumina
"CuPowder-BEL.as"	Copper powder

File format: Since the file is encrypted, it cannot be read with commercially-available spreadsheet software.

How to create a standard isotherm

1 Preparation of standard isotherm data

Read the adsorption volume (V_a / cm^3 (STP) 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 software.

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_a / cm^3 (STP) g^{-1}) to adsorption layer thickness (t / nm).
  Here, V_m is monolayer adsorption volume, and 0.354 is the monolayer thickness.

$$t = \frac{V_a}{V_m} \times 0.354 \tag{4}$$

- When to create a standard isotherm for the α_s plot:
  Convert adsorption volume (V / cm^3 (S.T.P.) g^{-1}) to α_s (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.

$$\alpha_s = \frac{V_a}{V_{0.4}} \tag{5}$$

3 Create a standard isotherm

Using a text editing software (such as “Note pad”), create a standard isotherm file. Create a file in a text format with items separated by commas.

→ P. 224 ”Data configuration of a standard isotherm”.

4 Save the standard isotherm file

Save the “standard isotherm data” you created in the directory where this software is installed.

→ file name extension P.224 “Data configuration of a standard isotherm”

→ standard isotherm data configuration table below

Data configuration of a standard isotherm for *t* plot analysis

Record configuration :

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+4	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	"N2",77.00,78.00
3	Header 3	Comment 2: Adsorbate liquid density, Number of molecules, Specific surface area of the standard sample, Adsorption volume at relative pressure 0.4	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

Measurement data file

Measurement data (adsorption isotherm data)

BELSORP series "measurement data" are stored at each measurement step. During measurement, a "measurement data" file can be opened using this analysis software, and data can be analyzed, so that you can always see the measurement conditions.

In addition, you can read the data using any commercial spreadsheet software after the measurement.

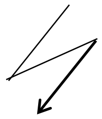
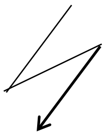
⚠ **Caution**

❗ **Do not use any other software (except this analysis software) to open the "measurement data file" while making measurement. The measurement software won't be able to keep writing data.**

The "measurement data" files are stored with file names that were specified during measurement. The file name extension is ".DAT" or ".NDAT". The record configuration produced by each model is shown below.

BELSORP 28SA, 18 and HP series (.DAT data file)

Record structure:

Record number	Record details
1	Header record 1
2	Header record 2
3	Header record 3
4	Header record 4
5	Adsorption measurement data header record
6	Adsorption measurement data record 
	Desorption measurement data header record
	Desorption measurement data record 

Each record details:

【Header record 1】

DATEMEAS	TIMEMEAS	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	SERIAL_NO	Measurement device serial No.	XXX～～～X	-	-
2	VERSION	Software version No.	XXX～～～X	-	-
3	DMY	“0.000000”	-	-	-

【Header record 2】

SW	Vs	Vd	EQT	ADS	TEMP1	TEMP2	P0	CS	ANLS1	ANLS2	ANLS3	ANLS3	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	SW	Sample weight (g)	9.99999	○	
2	Vs	Manifold volume (cm^3)	ZZ9.99999	○	
3	Vd	Sample free space (cm^3)	ZZ9.99999		○
4	EQT	Equilibrium time (Pa / min)	ZZ9.99999	○	
5	ADS	Adsorptive name	XXX～～～X	○	
6	TEMP1	Thermostatic chamber temperature (˚C)	ZZ9.9	○	
7	TEMP2	Adsorption temperature (K)	ZZ9.9	○	
8	P0	Saturation vapor pressure (Torr)	ZZZ9.999999	○	○
9	CS	Adsorptive cross section area (nm^2)	Z9.999	○	
10	ANLS1	“Sample molecular volume” (Written by the analysis software)	ZZ9.999	-	-
11	ANLS2	“Adsorptive molecular volume” (Written by the analysis software)	ZZ9.999	-	-
12	ANLS3	“Sample specific surface” (Written by the analysis software)	9.999E±Z9	-	-
13	ANLS4	Sample density (g / cm^3) (Written by the analysis software)	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 software. 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 software, the file will not be readable by previous versions of the analysis software.

【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

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	PI(n)	Introducing pressure (Torr)	ZZZ9.99999		○
2	PE(n)	Adsorption equilibrium pressure (Torr)	ZZZ9.99999		○
3	PE2(n)	Adsorption equilibrium pressure after closing valve (Torr)	ZZZ9.99999		○
4	P0(n)	Saturation vapor pressure (Torr)	ZZZ9.99999	○	○
5	V(n)	Total adsorption amount (cm^3(STP) / g)	ZZZ9.99999		Calculated value

- There are the same number of records as the number of adsorption measurement points.

【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

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	PI(n)	Introducing pressure (Torr)	ZZZ9.99999		○
2	PE(n)	Desorption equilibrium pressure (Torr)	ZZZ9.99999		○
3	PE2(n)	Desorption equilibrium pressure after closing valve (Torr)	ZZZ9.99999		○
4	P0(n)	Saturation vapor pressure (Torr)	ZZZ9.99999	○	○
5	V(n)	Total desorption amount (cm^3(STP) / g)	ZZZ9.99999		Calculated value

・There are the same number of records as the number of desorption measurement points.

Detail of the sample file:

→ Refer to the “Attached document 1: “Sample of a measurement data file (BELSORP 18, 28 series - .DAT)””, on P.261

BELSORP MINI, MAX, AQUA^3 series (.DAT data file)

Record structure:

Record number	Record details	
1	Device information	Title
2		
3		
4		Instrument S/N
5		Standard volume / cm^3
6	Measurement conditions	Title
7		
8		
9		Adsorptive name
10		Adsorption temperature / K
11		Adsorptive cross section area / nm^2
12		Adsorptive molecular weight
13		Equilibrium time / sec
14		Measurement mode
15	Sample information	Title
16		
17		
18		Sample weight / g
19		Comment 1
20		Comment 2
21		Comment 3
22		Comment 4
23		Sample specific surface / m^2 g^{-1}
24		Sample molecular weight
25		Sample density / g cm^{-3}

26	Time, free space, etc.	Title
27		
28		
29		Measurement start date
30		Measurement time
31		Dead volume slope
32		Dead volume intercept
33		Initial dead volume / cm^3
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			System property and version		
3			＝＝＝～～～＝		
4	Instrument S/N	Instrument serial number	XXX～～～X	○	
5	VS	Manifold volume / cm^3	9.999	○	

【Measurement conditions】

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	===〜〜〜=		
2			Measurement condition		
3			===〜〜〜=		
4	Adsorptive	Adsorptive name	XXX〜〜〜X	○	
5	Meas. Temp.	Adsorption temperature (K)	ZZ9.99	○	
6	Molecular cross sectional area	Adsorptive cross sectional area (nm^2)	9.999	○	
7	Molecular weight of adsorbate	Molecular weight of adsorbate	0.00 fixed	○	
8	Equilibrium time	Equilibrium time (sec)	ZZZ9	○	
9	Measured mode	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	Sample weight (g)	9.9999	○	
5	Comment1	Comment 1st line	XXX〜〜〜X	○	
6	Comment2	Comment 2nd line	XXX〜〜〜X	○	
7	Comment3	Comment 3rd line	XXX〜〜〜X	○	
8	Comment4	Comment 4th line	XXX〜〜〜X	○	
9	as	Sample specific surface (m^2 / g)	0.0000 fixed	○	
10	Molecular weight of adsobent	Molecular weight of sample	0.00 fixed	○	
11	-	Sample density (g / cm^3)	0.00 fixed		

【Time and free space】

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	===～～～=		
2			Time and dead volume		
3			===～～～=		
4	Date of measurement	Measurement start date	yy/mm/dd	○	
5	Time of measurement	Measurement time	hh:mm:ss	○	
6	Slope of dead volume	Slope of free space in measurement temperature	9.9999E+9	○	
7	Intercept of dead volume	Intercept of free space in measurement temperature	9.9999E+9	○	
8	Average dead volume	Average free space (cm^3)	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】

No.	Data name	Item detail	Format	Initial value	Measured value
1	I	Adsorption point No.	ZZ9		○
2	PeT	Adsorption equilibrium pressure p_e (kPa)	ZZ9.999		○
3	Ads_P0	Saturation vapor pressure p_0 (kPa)	ZZ9.999		○
4	Ads_Vd	Free space V_d (cm^3)	ZZ9.999		○
5	Ads_V	Adsorption amount V (cm^3(STP) / g)	ZZ9.999		○

- Adsorption data continues until the last record is 0.

【Desorption data】

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	===～～～=		
2			Desorption data		
3			===～～～=		
4			*2		
5	-	Desorption measurement data record	-		○

※2 "No." "Pe/kPa" "P0/kPa" "Vd/ml" "V/ml(STP) g-1"

【Desorption measurement data record】

No.	Data name	Item detail	Format	Initial value	Measured value
1	I	Desorption point No.	ZZ9		○
2	PeT	Desorption equilibrium pressure p_e (kPa)	ZZ9.999		○
3	Des_P0	Saturation vapor pressure p_0 (kPa)	ZZ9.999		○
4	Des_Vd	Free space V_d (cm^3)	ZZ9.999		○
5	Des_V	Desorption amount V (cm^3(STP) / g)	ZZ9.999		○

- Desorption data continues until the last record is 0.

Detail of sample file:

→ Refer to the “Attached document 2: “Sample of a measurement data file (BELSORP MINI series - .DAT)””, on P.262

BELSORP MAX II / G / X, MINI X series (.NDAT data file)

Record structure:

Record number	Record details
1	Header record
2	Adsoption measurement header record 1
3	Adsoption measurement header record 2
4	Adsoption measurement data record ↯
5	Desoption measurement header record 1
6	Desoption measurement header record 2
7	Desoption measurement data record ↯

- The items in No. 4 are repeated as many as adsorption measurement data points (including cutoff).
- The items in No. 7 are repeated as many as desorption measurement data points (including cutoff).

Each record detail:

【Header record】

- Field details

The measurement conditions for the relevant data are saved.

【Adsorption measurement header record 1】

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	--- ∼∼∼ ---		
2			Adsorption side		
3			--- ∼∼∼ ---		
4	No. of ads. measurement point	Number of adsorption measurement point	ZZ9	○	

【Adsorption measurement header record 2】

N	Pi_i	Pi_e	Vs	Vd	Pe	P0	BT	AT	(VD)	(TM)	DVd	V	V1	V2	V3	V4	ZR_Pi_i	ZR_Pi_e

ZR_Pe	ZL_Pe	SLOPE	In_time	In_Press	Pe2	Ti	Te	Te2	n1	n2	n3	n4	VdRT(cm3)	Vsce2n-1(cm3)

ZRke2n-1(-)	Vscin(cm3)	ZRkin(-)	Vscen(cm3)	Vdcen(cm3)	ZRken(-)	ZLken(-)	VLken(cm3)	ET	Mask	CrLf

The header of the adsorption measurement is saved. See 【Adsorption measurement data record】 for the contents of each item.

【Adsorption measurement data record】

No.	Data name	Item detail	Format	Initial value	Measured value
1	N	Adsorption / Desorption point No. (Space shows cutoff dosing)	ZZ9		○
2	Pi_i	Pressure in manifold before dosing gas (Pa)	ZZZ9.99999		○
3	Pi_e	Pressure in manifold after dosing gas (Pa)	ZZZ9.99999		○
4	Vs	Manifold volume (cm^3)	ZZZ9.99999		○
5	Vd	Free space volume (cm^3)	ZZZ9.99999		○
6	Pe	Equilibrium pressure (Pa) (without thermal transpiration correction)	ZZZ9.99999		○
7	P0	Saturated vapor pressure (Pa)	ZZZ9.99999		○
8	BT	Manifold temperature (K)	ZZZ9.99		○
9	AT	Adsorption temperature (K)	ZZZ9.999		○
10	(VD)	Pressure in reference cell (Pa)	ZZZ9.99999		○
11	(TM)	Elapsed time after setting temperature device (sec)	ZZZ9.99999		○
12	DVd	Free space change (cm^3)	ZZZ9.99999		○
13	V	Amount adsorbed (cm^3 (STP) g^{-1})	ZZZ9.99999		○
14	V1	Parameters for calculating amount adsorbed	ZZZ9.99999		○
15	V2		ZZZ9.99999		○
16	V3		ZZZ9.99999		○

17	V4		ZZZ9.99999	○
18	ZR_Pi_i	Compression factor at pressure in manifold before dosing gas	ZZZ9.99999	○
19	ZR_Pi_e	Compression factor at pressure in manifold after dosing gas	ZZZ9.99999	○
20	ZR_Pe	Compression factor at equilibrium pressure (at manifold temperature)	ZZZ9.99999	○
21	ZL_Pe	Compression factor at equilibrium pressure (at adsorption temperature)	ZZZ9.99999	○
22	SLOPE	Not used	-	-
23	In_time		-	-
24	In_Press		-	-
25	Pe2	Pressure with closing valve between manifold and sample after getting equilibrium pressure (Pa)	ZZZ9.99999	○
26	Ti	Manifold temperature before dosing gas (K)	ZZZ9.99	○
27	Te	Manifold temperature after dosing gas (K)	ZZZ9.99	○
28	Te2	Manifold temperature with closing valve between manifold and sample after getting equilibrium pressure (K)	ZZZ9.99	○
29	n1	Not used	-	-
30	n2		-	-
31	n3		-	-
32	n4		-	-
33	VdRT(cm3)		-	-
34	Vsce2n-1(cm3)		-	-
35	ZRke2n-1(-)		-	-
36	Vscin(cm3)		-	-
37	ZRkin(-)		-	-

38	Vscen(cm3)			-	-
39	Vdcen(cm3)			-	-
40	ZRken(-)			-	-
41	ZLken(-)			-	-
42	VLken(cm3)			-	-
43	ET	Elapsed time	XX:XX:XX		○
44	Mask	Data with mask fuction	X		○

Some layouts and contents may vary depending on measurement conditions and instrument.

【Desorption measurement header record 1】

No.	Data name	Item detail	Format	Initial value	Measured value
1	DMY	Title	--- ～～～ ---		
2			Desorption side		
3			--- ～～～ ---		
4	No. of des. measurement point	Number of desorption measurement point	ZZ9	○	

【Desorption measurement header record 2】

The header of the desorption measurement is saved. See 【Adsorption measurement data record】 for the contents of each item.

【Desorption measurement data record 2】

See 【Adsorption measurement data record】 for the contents of each item.

Detail of sample file:

→ Refer to the “Attached document 3: “Sample of a measurement data file (BELSORP MAX II / G / X, MINI X series - .NDAT)””, on P.264

Measurement data (adsorption kinetics data)

BELSORP series can save the data which involve the pressure change against the time for the adsorption isotherm measurement (Option).

In addition, you can read the data using any commercial spreadsheet software after the measurement.

⚠ Caution

Do not use any other software (except this analysis software) to open the "measurement data file" while making measurement. The measurement software won't be able to keep writing data.

The "kinetics measurement data" files are stored with file names that were specified during measurement. The file name extension is ".RAT" or ".NRAT". The record configuration produced by each model is shown below.

BELSORP 28SA, 18 series (.RAT data file)

Record structure:

Record number	Record details
1	Header record 1
2	Header record 2
3	Header record 3
4	Header record 4
5	Number of the saving point between adsorption rate measurement
6	nth-Adsorption kinetic data header
7	nth-Adsorption kinetic measurement data record
8	nth-Adsorption kinetic measurement data footer
9	nth-Adsorption equilibrium data

・The items in No. 6 ~ 9 are repeated as many as adsorption measurement data points.

Each record details:

【Header record 1】

DATEMEAS	TIMEMEAS	COMMENT1	COMMENT2	COMMENT3	COMMENT4	0	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	0	-	0 fixed	-	-

【Header record 2】

SERIAL_NO	INSTRUMENT	VERSION_NO	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	SERIAL_NO	Measurement device Serial No.	XXX～～～X	○	-
2	INSTRUMENT	Name of measurement instrument	XXX～～～X	○	-
3	VERSION_NO	-	-	-	-

【Header record 3】

SW	Vs	Vd	EQT	ADS	TEMP1	TEMP2	P0	CS	VDRT	VDD	0	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	SW	Sample weight (g)	9.99999	○	
2	Vs	Manifold volume (cm^3)	ZZ9.99999	○	
3	Vd	Sample free space (cm^3)	ZZ9.99999		○
4	EQT	Equilibrium time (Pa / min)	ZZ9.99999	○	
5	ADS	Adsorptive name	XXX～～～X	○	
6	TEMP1	Thermostatic chamber temperature (˚C)	ZZ9.9	○	
7	TEMP2	Measurement temperature (K)	ZZ9.9	○	
8	P0	Saturation vapor pressure (Torr)	ZZZ9.999999	○	○
9	CS	Adsorptive cross sectional area (nm^2)	Z9.999	○	
10	VDRT	Free space in the room temperature (cm^3)	ZZ9.999	○	
11	VDD	Corrected free space in the measurememt temperature (cm^3)	ZZ9.999		○
12	0	-	0 固定	-	-

【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	○	

【Number of the saving points for adsorption rate measurement】

K	CrLf

・ Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	K	Number of the saving points for adsorption rate measurement	ZZ9	○	○

【nth-Adsorption kinetic data header】

PI(n)	CrLf

・ Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	PI(n)	Introducing pressure (Torr)	ZZZ9.99999		○

【nth-Adsorption kinetic measurement data record】

TIME	L	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	TIME	Time (sec.)	ZZZ9.99999		○
2	C	Concentration for each time (Torr) Same as Equation (14) in "Adsorption rate analysis". The Last value shows the equilibrium pressure (P_{en}) (Torr).	ZZZ9.99999		○

【nth-Adsorption kinetic measurement data footer】

-999	-999	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	-999	-	-999 fixed	-	-
2	-999	-	-999 fixed	-	-

【nth-Adsorption equilibrium data】

EQU_PRESS	VOL_ADS	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	EQU_PRESS	Equilibrium pressure after the valve is closed (P_{e2n}). (Torr)	ZZZ9.99999		○
2	VOL_ADS	Adsorption amount in equilibrium pressure (cm^3 (STP) / g)	ZZZ9.99999		○

Detail of the sample file:

→ Refer to the "Attached document 4: "Sample of a kinetic data file (BELSORP 28SA, 18 series - .RAT)"", on P.266.

BELSORP HP (.RAT data file)

Record structure:

Record number	Record details
1	Header record 1
2	Header record 2
3	Header record 3
4	Header record 4
5	Number of the saving point between adsorption rate measurement
6	nth-Adsorption kinetic measurement data record
7	nth-Adsorption kinetic measurement data footer
8	nth-Adsorption equilibrium data
	↯

- The items in No. 6 ~ 8 are repeated as many as adsorption measurement data points.

Each record details:

【Header record 1】

BLANK	DATEMEAS	TIMEMEAS	COMMENT1	COMMENT2	COMMENT3	COMMENT4	0	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	BLANK	-	0 fixed	-	-
2	DATEMEAS	Measurement start date	“YY/MM/DD”		○
3	TIMEMEAS	Measurement time	“hh:mm:ss”		○
4	COMMENT1	Comment 1st line	XXX～～～X	○	
5	COMMENT2	Comment 2nd line	XXX～～～X	○	
6	COMMENT3	Comment 3rd line	XXX～～～X	○	
7	COMMENT4	Comment 4th line	XXX～～～X	○	
8	0	-	0 fixed	-	-

【Header record 2】

SERIAL_NO	VERSION_NO	0	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	SERIAL_NO	Measurement instrument serial No.	XXX～～～X	○	-
2	VERSION_NO	"0.000000"	-	-	-
3	0	-	0 fixed	-	-

【Header record 3】

SW	Vs	Vd	EQT	ADS	TEMP1	TEMP2	P0	CS	0	0	0	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	SW	Sample weight (g)	9.99999	○	
2	Vs	Manifold volume for 1st point (cm^3)	ZZ9.99999	○	
3	Vd	Sample free space (cm^3)	ZZ9.99999		○
4	EQT	Equilibrium time (Pa/min)	ZZ9.99999	○	
5	ADS	Adsorptive name	XXX～～～X	○	
6	TEMP1	Thermostatic chamber temperature (˚C)	ZZ9.9	○	
7	TEMP2	Measurement temperature (K)	ZZ9.9	○	
8	P0	Saturation vapor pressure (Torr)	ZZZ9.999999	○	○
9	CS	Adsorptive cross sectional area (nm^2)	Z9.999	○	
10	0	-	0 fixed	-	-
11	0	-	0 fixed	-	-
12	0	-	0 fixed	-	-

【Header record 4】

BLANK	0	0	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	BLANK	-	“” fixed	-	-
2	0	-	0 fixed	-	-
3	0	-	0 fixed	-	-

【Number of the saving points for adsorption rate measurement】

K	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	K	Number of the saving points for adsorption rate measurement	ZZ9	○	○

【nth-Adsorption kinetic measurement data record】

TIME	C	C0n	Cen	Pt	Pi	Vs	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	TIME	Time (sec.)	ZZZ9.99999		○
2	C	Concentration for each time (Torr) Same as Equation (14) in "Adsorption rate analysis". The Last value shows the equilibrium pressure (P_{en}) (Torr)	ZZZ9.99999		○
3	C0n	Initial concentration on arbitrary point (Torr) Same as Equation (13) in "Adsorption rate analysis".	ZZZ9.99999		○
4	Cen	Equilibrium concentration on arbitrary point (Torr)	ZZZ9.99999		○
5	Pt	Pressure for each time (Torr) The Last value shows the equilibrium pressure (P_{en}) (Torr)	ZZZ9.99999		○
6	Pi	Introducing pressure on arbitrary point (Torr)	ZZZ9.99999		○
7	Vs	Manifold volume (cm^3)	ZZZ9.99999		○

【nth-Adsorption kinetic measurement data footer】

-999	-999	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	-999	-	-999 fixed	-	-
2	-999	-	-999 fixed	-	-

【nth-Adsorption equilibrium data】

EQU_PRESS	VOL_ADS	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	EQU_PRESS	Equilibrium pressure after the valve is closed (P_{e2n}). (Torr)	ZZZ9.99999		○
2	VOL_ADS	Adsorption amount in equilibrium pressure (cm^3 (STP) / g)	ZZZ9.99999		○

Detail of the sample file

→ Refer to the "Attached document 5: "Sample of a kinetic data file (BELSORP HP - .RAT)"", on P.267.

BELSORP AQUA^3, MAX series (.RAT data file)

Record structure:

Record number	Record details
1	Header record 1
2	Header record 2
3	Header record 3
4	Header record 4
5	Number of the saving point between adsorption rate measurement
6	nth-Adsorption rate measurement data record
7	nth-Adsorption rate measurement data footer
8	nth-Adsorption equilibrium data

- The items in No. 6 ~ 8 are repeated as many as adsorption measurement data points.

Each record details:

【Header record 1】

BLANK	DATEMEAS	TIMEMEAS	COMMENT1	COMMENT2	COMMENT3	COMMENT4	0	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	BLANK	-	0 fixed	-	-
2	DATEMEAS	Measurement start date	“YY/MM/DD”		○
3	TIMEMEAS	Measurement time	“hh:mm:ss”		○
4	COMMENT1	Comment 1st line	XXX～～～X	○	
5	COMMENT2	Comment 2nd line	XXX～～～X	○	
6	COMMENT3	Comment 3rd line	XXX～～～X	○	
7	COMMENT4	Comment 4th line	XXX～～～X	○	
8	0	-	0 fixed	-	-

【Header record 2】

SERIAL_NO	INSTRUMENT	VERSION_NO	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	SERISAL_NO	Measurement instrument serial No.	XXX～～～X	○	-
2	INSTRUMENT	Name of measurement instrument	XXX～～～X	○	-
3	VERSION_NO	"0.000000"	-	-	-

【Header record 3】

SW	Vs	Vd	EQT	ADS	TEMP1	TEMP2	P0	0	0	0	0	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	SW	Sample weight (g)	9.99999	○	
2	Vs	Manifold volume (cm^3)	ZZ9.99999	○	
3	Vd	Sample free space (cm^3)	ZZ9.99999		○
4	EQT	Equilibrium time (Pa/min)	ZZ9.99999	○	
5	ADS	Adsorptive name	XXX～～～X	○	
6	TEMP1	Thermostatic chamber temperature (˚C)	ZZ9.9	○	
7	TEMP2	Measurement temperature (K)	ZZ9.9	○	
8	P0	Saturation vapor pressure (kPa)	ZZZ9.999999	○	○
9	0	-	0 fixed	-	-
10	0	-	0 fixed	-	-
11	0	-	0 fixed	-	-
12	0	-	0 fixed	-	-

【Header record 4】

BLANK	0	0	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	BLANK	-	“” fixed	-	-
2	0	-	0 fixed	-	-
3	0	-	0 fixed	-	-

【Number of the saving points for adsorption rate measurement】

K	CrLf

・Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	K	Number of the saving points for adsorption rate measurement	ZZ9	○	○

【nth-Adsorption rate measurement data record】

TIME	C	C0n	Cen	Pt	PVdt	Vdcor	DVd	PVdncor	Vd	Vdcor	CrLf

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	TIME	Time (sec.)	ZZZ9.99999		○
2	C	Concentration for each time (kPa) Same as Equation (14) in the chapter of "Adsorption rate analysis". The last value shows the equilibrium pressure (P_{en}) (kPa)	ZZZ9.99999		○
3	C0n	Initial concentration on arbitrary point (kPa) Same as Equation (13) in the chapter of "Adsorption rate analysis".	ZZZ9.99999		○
4	Cen	Equilibrium concentration on arbitrary point (kPa)	ZZZ9.99999		○
5	Pt	Pressure for each time of Vs part (kPa) The Last value shows the equilibrium pressure (P_{en}) (kPa)	ZZZ9.99999		○
6	PVdt	Pressure for each time of Vd part with thermal transpiration (kPa)	ZZZ9.99999		○
7	Vdcor	Free space with non-ideality correction (cm^3)	ZZZ9.99999		○
8	DVd	Free space change for each time (cm^3)	ZZZ9.99999		○
9	PVdncor	Pressure for each time of Vd part without thermal transpiration (kPa)	ZZZ9.99999		○
10	Vd	Free space without non-ideality correction (cm^3)	ZZZ9.99999		○
11	Vdcor	Free space with non-ideality correction (cm^3) Same as item 7 (Vdcor)	ZZZ9.99999		○

【nth-Adsorption rate measurement data footer】

-999	-999	CrLf

・ Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	-999	-	-999 fixed	-	-
2	-999	-	-999 fixed	-	-

【nth-Adsorption equilibrium data】

EQU_PRESS	VOL_ADS	ADS_PE	Pe_T2	CrLf

・ Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	EQU_PRESS	Equilibrium pressure of Vd part with thermal transpiration (kPa)	ZZZ9.99999		○
2	VOL_ADS	Adsorption amount in equilibrium pressure (cm^3 (STP) / g)	ZZZ9.99999		○
3	ADS_PE	Equilibrium pressure for each time of Vd part without thermal transpiration (kPa)	ZZZ9.99999		○
4	Pe_T2	Equilibrium pressure for each time of Vd part with thermal transpiration (kPa)	ZZZ9.99999		○

Detail of the sample file:

→ Refer to the “Attached document 6: “Sample of a kinetic data file (BELSORP AQUA3, MAX series - .RAT)””, on P.268.

BELSORP MAX II / G / X (.NRAT data file)

Record structure:

Record number	Record details
1	Header record
2	Adsorption rate measurement header record
3	Adsorption rate measurement data record
4	Adsorption rate measurement data footer record
5	Adsorption rate measurement equilibrium data record
	↯

- The items in No. 3 ~ 5 are repeated as many as adsorption measurement data points.

Each record details:

【Header record】

- Field details

The measurement conditions for the relevant data are saved.

【Adsorption rate measurement header record】

TIME	C	C0n	Cen	Pvsin	Pvst	Pvdt	Vs	Vd	dVd	Pvdt Thermal YES	Vd-Non ideality No	Vd-Non ideality YES	Vs-Non ideality No	Vs-Non idelaity YES	CrLf

The header of the adsorption rate measurement is saved. See 【Adsorption rate measurement data record】 for the contents of each item.

【Adsorption rate measurement data record】

- Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	TIME	Time (sec.)	ZZZ9.999		○
2	C	Concentration for each time (kPa) Same as Equation (14) in the chapter of "Adsorption rate analysis". The last value shows the equilibrium pressure (P_{en}) (kPa)	ZZZ9.99999		○

3	C0n	Initial concentration on arbitrary point (kPa) Same as Equation (13) in the chapter of "Adsorption rate analysis".	ZZZ9.99999	○
4	Cen	Equilibrium concentration on arbitrary point (kPa)	ZZZ9.99999	○
5	Pvsin	Pressure before dosing gas (kPa)	ZZZ9.99999	○
6	Pvst	Pressure for each time of Vma part (kPa) The Last value shows the equilibrium pressure (P_{en}) (kPa)	ZZZ9.99999	○
7	Pvdt	Pressure for each time of Vfs part with thermal transpiration (kPa)	ZZZ9.99999	○
8	Vs	Manifold temperature with non-ideality correction (cm^3)	ZZZ9.99999	○
9	Vd	Fress space with non-ideality correction (cm^3)	ZZZ9.99999	○
10	dvd	Free space change for each time (cm^3)	ZZZ9.99999	○
11	Pvdt Thermal YES	Pressure for each time of Vfs part with thermal transpiration (kPa)	ZZZ9.99999	○
12	Vd-Non ideality No	Free space with non-ideality correction (cm^3)	ZZZ9.99999	○
13	Vd-Non ideality YES	Free space without non-ideality correction (cm^3)	ZZZ9.99999	○
14	Vs-Non ideality No	Manifold volume with non-ideality correction (cm^3)	ZZZ9.99999	○
15	Vs-Non idelaity YES	Manifold without non-ideality correction (cm^3)	ZZZ9.99999	○
16	-	Pressure in reference cell (Pa)	ZZZ9.99999	○
17	-	Elapsed time (sec)	ZZZ9.99999	○
18	-	Pressure for each time in Vfs part with thermal transpiration (kPa)	ZZZ9.99999	○
19	-	Manifold temperature (K)	ZZZ9.99999	○
20	-	Saturated vapor pressure (Pa)	ZZZ9.99999	○

21	-	Pressure at the timing of dosing gas (kPa)	ZZZ9.99999		○
22	-	Pressure in Vfs part at the timing of dosing gas (kPa)	ZZZ9.99999		○
23	-	Free space with non-idality correction at the timing of dosing gas (cm^3)	ZZZ9.99999		○
24	-	Free space change at the timing of dosing gas (cm^3)	ZZZ9.99999		○
25	-	Pressure in reference cell at the timing of dosing gas (Pa)	ZZZ9.99999		○
26	-	Elapsed time at the timing of dosing gas (sec)	ZZZ9.99999		○
27	-	Pressure in Vfs part at the timing of dosing gas (Pa)	ZZZ9.99999		○
28	-	Manifold temperature at the timing of dosing gas (K)	ZZZ9.99999		○
29	-	Vapor pressure at the timing of dosing gas (Pa)	ZZZ9.99999		○

Some layouts and contents may vary depending on measurement conditions and instrument.

【Adsorption rate measurement data footer record】

-999	-999	CrLf

・ Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	-999	-	-999 fixed	-	-
2	-999	-	-999 fixed	-	-

【Adsorption rate measurement equilibrium data record】

EQU_PRESS	VOL_ADS	ADS_PE	Pe_T2	CrLf

・ Field details

No.	Data name	Item detail	Format	Initial value	Measured value
1	EQU_PRESS	Equilibrium pressure of Vfs part with thermal transpiration (kPa)	ZZZ9.99999		○

2	VOL_ADS	Adsorption amount in equilibrium pressure (cm^3 (STP) / g)	ZZZ9.99999	○
3	ADS_PE	Equilibrium pressure for each time of Vfs part without thermal transpiration (kPa)	ZZZ9.99999	○
4	Pe_T2	Equilibrium pressure for each time of Vfs part with thermal transpiration (kPa)	ZZZ9.99999	○

Detail of the sample file:

→ Refer to the "Attached document 7: "Sample of a kinetic data file (BELSORP MAX II / G / X - .NRAT)"", on P.269.

Attached document 1: “Sample of a measurement data file (BELSORP 18, 28 series - .DAT)”

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 (BELSORP MINI series - .DAT)”

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 slope:”     -1.547E-06
32  “ Dead volume intercept:”             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
```

```
3       0.30627    103.35    13.668    13.92
4       2.6323     103.29    13.653    16.056
5       4.8454     103.24    13.639    16.629
                             ⋮
50      103.29     103.44    13.299    543.96
0       0          0         0         0
====================
Desorption data
====================
"No."   "Pe/kPa"   "P0/kPa"  "Vd/ml"   "V/ml(STP) g-1"
1       100.53     103.34    13.281    518.6
2       100.17     103.38    13.269    494.5
3       99.939     103.41    13.254    467.91
4       99.757     103.47    13.239    441.73
5       99.593     103.47    13.225    416.01
                             ⋮
34      29.968     103.12    12.547    24.388
0       0          0         0         0
```

Attached document 3: “Sample of a measurement data file (BELSORP MAX II / G / X, MINI X series - .NDAT)”

Record number

```
  1  ====================

  2  Instrument information

  3  ====================

  4  Instrument name                BELSORP-miniX

  5  Instrument S/N                 001

  6  Software version               Version 1.1.3.1

  7  Vs_0(ml)     12.4943

  8  Vs_1(ml)     0

  9  ====================

 10  User information

 11  ====================

              ⋮

214  ====================

215  Measurement result

216  ====================

217  ----------------------------------------

218  Adsorption side

219  ----------------------------------------

220  No of ads. measurement point           37

     N            Pi_i         Pi_e         Vs           Vd           Pe           P0           BT           AT           (VD)         (TM)
     DVd          V            V1           V2           V3           V4           ZR_Pi_i      ZR_Pi_e      ZL           SLOPE        In_time
220  In_Press     Pe2          Ti           Te           Te2          n1           n2           n3           n4           VdRT(cm3)
     Vsce2n-1(cm3)             ZRke2n-1(-)  Vscin(cm3)   ZRkin(-)     Vscen(cm3)   Vdcen(cm3)   ZRken(-)     ZLken(-)     VLken(cm3)   ET
     Mask

     0            0            0            12.4943      15.1800      0            102722.591   0            0            0            0
     0            0            0            0            0            0            1            1            1
221               0            0            0            298.641
                                                                                                                                     1:25:12

     1            5554.0361    87.00268     12.4943      15.15584     23.15420     102767.72    298.667      77.35        53912.21     3888.438
     -0.167903    3.0370069    228.6977     0            1.129021     0            1            1            0.999990
222               0            298.677      298.677      0
                                                                                                                                     1:34:55

              ⋮

294  ----------------------------------------

295  Desorption side

296  ----------------------------------------

     N            Pi_i         Pi_e         Vs           Vd           Pe           P0           BT           AT           (VD)         (TM)
     DVd          V            V1           V2           V3           V4           ZR_Pi_i      ZR_Pi_e      ZL           SLOPE        In_time
297  In_Press     Pe2          Ti           Te           Te2          n1           n2           n3           n4           VdRT(cm3)
     Vsce2n-1(cm3)             ZRke2n-1(-)  Vscin(cm3)   ZRkin(-)     Vscen(cm3)   Vdcen(cm3)   ZRken(-)     ZLken(-)     VLken(cm3)   ET
     Mask

                  94443.524    100013.58    12.4943      14.881726    101171.34    102476.69    298.182      77.35        56228.623    52804.25
298  -0.869009    579.2298     -3285.315    5070.8865    5049.2795    0            1            1            0.9567796
                  0            298.28       298.273      0
                                                                                                                                     15:10:11
              ⋮
```

```
====================
AFSM2 parameters
====================
Cell ID       TEST1
REF Cell ID  TEST4
Adsorptive  N2
Ads. Temp.  77.35
        ⋮
```

Some layouts and contents may vary depending on measurement conditions and instrument.

Attached document 4: “Sample of a kinetic data file (BELSORP 28SA, 18 series - .RAT)”

Record number

```
 1    "17/04/05","1:21:17","170405_carbonblack","","","Sample cell leak amount：0.012Pa/min",0
 2    "18-219","BELSORP 18",1.2
 3    .0123,42.88,36.2248733912415,300,"N2",50,77.35,0,.195,16.4806073329009,0,0
 4    "",0,0
 5    10
 6    0.03762
 7    1 , 0.03457
 8    2 , 0.03304
 9    3 , 0.03243
10    4 , 0.03213
11    5 , 0.03182
12    6 , 0.03152
13    8 , 0.03091
14    10 , 0.03030
15    13 , 0.02969
16    16 , 0.02877
17    20 , 0.02786
18    25 , 0.02663
19    32 , 0.02511
20    40 , 0.02328
21    50 , 0.02145
          ⋮
30    398 , 0.00191
31    501 , 0.00161
32    631 , 0.00161
33    708 , 0.00153
34    -999 , -999
35    0.00161,0.13490
36    15.34415
37    1 , 13.48289
38    2 , 13.26931
39    3 , 13.05572
40    4 , 12.87265
          ⋮
```

Attached document 5: "Sample of a kinetic data file (BELSORP HP - .RAT)"

Record number

```
 1   ,"16/06/24","2:12:28","","","","Sample cell leak amount：0.550Pa/min",0
 2   "HP-000","1.4.8",0
 3   .6247,24.661,10.3336749509509,300,"N2",24.99,298.15,7500636.80412835,0,0,0,0
 4   "",0,0
 5   10
 6   1 , 8.5510872E+0, 7.5463235E+0, 6.3974471E+0, 8.5510872E+0, 1.0708452E+1,  24.661
 7   2 , 7.3415351E+0, 7.5463235E+0, 6.3974471E+0, 7.3415351E+0, 1.0708452E+1,  24.661
 8   3 , 6.8950561E+0, 7.5463235E+0, 6.3974471E+0, 6.8950561E+0, 1.0708452E+1,  24.661
 9   4 , 6.6636988E+0, 7.5463235E+0, 6.3974471E+0, 6.6636988E+0, 1.0708452E+1,  24.661
10   5 , 6.5459907E+0, 7.5463235E+0, 6.3974471E+0, 6.5459907E+0, 1.0708452E+1,  24.661
11   6 , 6.4688716E+0, 7.5463235E+0, 6.3974471E+0, 6.4688716E+0, 1.0708452E+1,  24.661
12   8 , 6.4201648E+0, 7.5463235E+0, 6.3974471E+0, 6.4201648E+0, 1.0708452E+1,  24.661
13   10 , 6.4079881E+0, 7.5463235E+0, 6.3974471E+0, 6.4079881E+0, 1.0708452E+1,  24.661
14   13 , 6.3998703E+0, 7.5463235E+0, 6.3974471E+0, 6.3998703E+0, 1.0708452E+1,  24.661
15   16 , 6.3998703E+0, 7.5463235E+0, 6.3974471E+0, 6.3998703E+0, 1.0708452E+1,  24.661
16   20 , 6.3998703E+0, 7.5463235E+0, 6.3974471E+0, 6.3998703E+0, 1.0708452E+1,  24.661
17   25 , 6.3958114E+0, 7.5463235E+0, 6.3974471E+0, 6.3958114E+0, 1.0708452E+1,  24.661
18   32 , 6.3958114E+0, 7.5463235E+0, 6.3974471E+0, 6.3958114E+0, 1.0708452E+1,  24.661
            ⋮
30   200 , 6.4039292E+0, 7.5463235E+0, 6.3974471E+0, 6.4039292E+0, 1.0708452E+1,  24.661
31   251 , 6.3917525E+0, 7.5463235E+0, 6.3974471E+0, 6.3917525E+0, 1.0708452E+1,  24.661
32   316 , 6.3958114E+0, 7.5463235E+0, 6.3974471E+0, 6.3958114E+0, 1.0708452E+1,  24.661
33   398 , 6.3998703E+0, 7.5463235E+0, 6.3974471E+0, 6.3998703E+0, 1.0708452E+1,  24.661
34   501 , 6.3998703E+0, 7.5463235E+0, 6.3974471E+0, 6.3998703E+0, 1.0708452E+1,  24.661
35   -999 , -999
36   6.3974471E+0,0.58198
37   1 , 2.6852667E+1, 2.6352773E+1, 2.3399027E+1, 2.6852667E+1, 3.4714634E+1,  24.661
38   2 , 2.4587800E+1, 2.6352773E+1, 2.3399027E+1, 2.4587800E+1, 3.4714634E+1,  24.661
39   3 , 2.3743549E+1, 2.6352773E+1, 2.3399027E+1, 2.3743549E+1, 3.4714634E+1,  24.661
40   4 , 2.3544663E+1, 2.6352773E+1, 2.3399027E+1, 2.3544663E+1, 3.4714634E+1,  24.661
            ⋮
```

Attached document 6: “Sample of a kinetic data file (BELSORP AQUA^3, MAX series - .RAT)”

Record number

```
  1   ,"12/02/08","1:02:57","Carbon black","","","Sample cell leak amount: port",0
  2   "000000","BELSORP MAX","Ver1.3.9"
  3   .2091,24.619045,27.3319186872223,0,"N2",313.15,77.35,103.091672574657,0,0,0,0
  4   "",0,0
  5   1,120,30,30,30,60
  6   0.297 , 3.1566345E+0, 1.5403829E+0, 1.7141816E-2, 3.1566345E+0, 5.8022392E-5, 2.7324455E+1, -1.7841809E-1, 2.9586771E-5, 2.7324454E+1, 2.7324455E+1
  7   0.641 , 3.0714081E+0, 1.5403829E+0, 1.7141816E-2, 3.0714081E+0, 1.2714644E-4, 2.7324455E+1, -1.7841809E-1, 6.5758167E-5, 2.7324454E+1, 2.7324455E+1
  8   0.719 , 2.7548529E+0, 1.5403829E+0, 1.7141816E-2, 2.7548529E+0, 1.3740430E-3, 2.7326239E+1, -1.7664138E-1, 8.0546236E-4, 2.7326231E+1, 2.7326239E+1
  9   0.782 , 2.6574513E+0, 1.5403829E+0, 1.7141816E-2, 2.6574513E+0, 1.6959954E-3, 2.7326240E+1, -1.7664138E-1, 1.0176027E-3, 2.7326231E+1, 2.7326240E+1
 10   0.922 , 2.5559913E+0, 1.5403829E+0, 1.7141816E-2, 2.5559913E+0, 2.0179764E-3, 2.7326242E+1, -1.7664138E-1, 1.2373523E-3, 2.7326231E+1, 2.7326242E+1
 11   1.047 , 2.4504729E+0, 1.5403829E+0, 1.7141816E-2, 2.4504729E+0, 2.6618654E-3, 2.7326246E+1, -1.7664138E-1, 1.6981354E-3, 2.7326231E+1, 2.7326246E+1
 12   1.188 , 2.2434945E+0, 1.5403829E+0, 1.7141816E-2, 2.2434945E+0, 3.3056830E-3, 2.7326249E+1, -1.7664138E-1, 2.1850987E-3, 2.7326231E+1, 2.7326249E+1
 13   1.266 , 2.1298593E+0, 1.5403829E+0, 1.7141816E-2, 2.1298593E+0, 3.6276290E-3, 2.7328028E+1, -1.7486438E-1, 2.4376488E-3, 2.7328008E+1, 2.7328028E+1
 14   1.563 , 2.0202825E+0, 1.5403829E+0, 1.7141816E-2, 2.0202825E+0, 3.9495989E-3, 2.7326253E+1, -1.7664138E-1, 2.6958307E-3, 2.7326231E+1, 2.7326253E+1
 15   1.704 , 1.8457713E+0, 1.5403829E+0, 1.7141816E-2, 1.8457713E+0, 1.8338266E+0, 2.7336425E+1, -1.7664138E-1, 1.8337977E+0, 2.7326231E+1, 2.7336425E+1
 16   1.829 , 1.8133041E+0, 1.5403829E+0, 1.7141816E-2, 1.8133041E+0, 1.8093688E+0, 2.7336289E+1, -1.7664138E-1, 1.8093395E+0, 2.7326231E+1, 2.7336289E+1
 17   1.907 , 1.7889537E+0, 1.5403829E+0, 1.7141816E-2, 1.7889537E+0, 1.7726822E+0, 2.7336085E+1, -1.7664138E-1, 1.7726523E+0, 2.7326231E+1, 2.7336085E+1
 18   2.11 , 1.7524281E+0, 1.5403829E+0, 1.7141816E-2, 1.7524281E+0, 1.7482244E+0, 2.7335949E+1, -1.7664138E-1, 1.7481941E+0, 2.7326231E+1, 2.7335949E+1
          ⋮
861   398.157 , 1.7200995E-2, 1.5403829E+0, 1.7141816E-2, 1.7200995E-2, 1.7101121E-2, 2.7299706E+1, -2.0326110E-1, 1.5456481E-2, 2.7299611E+1, 2.7299706E+1
862   430.141 , 1.7200995E-2, 1.5403829E+0, 1.7141816E-2, 1.7200995E-2, 1.7141816E-2, 2.7296162E+1, -2.0680540E-1, 1.5498348E-2, 2.7296067E+1, 2.7296162E+1
863   464.204 , 1.7160288E-2, 1.5403829E+0, 1.7141816E-2, 1.7160288E-2, 1.7141816E-2, 2.7292619E+1, -2.1034853E-1, 1.5498348E-2, 2.7292524E+1, 2.7292619E+1
864   501.297 , 1.7241702E-2, 1.5403829E+0, 1.7141816E-2, 1.7241702E-2, 1.7101121E-2, 2.7289077E+1, -2.1389048E-1, 1.5456481E-2, 2.7288982E+1, 2.7289077E+1
865   513 , 1.7200995E-2, 1.5403829E+0, 1.7141816E-2, 1.7200995E-2, 1.7141816E-2, 2.7289077E+1, -2.1389048E-1, 1.5498348E-2, 2.7288982E+1, 2.7289077E+1
866   -999 , -999
867   1.5469041E-2,3.25893,1.7113330E-2,1.5469041E-2
868   0.203 , 1.2485160E+0, 6.0731991E-1, 2.3083366E-2, 1.2485160E+0, 3.8832542E-2, 2.7285656E+1, -2.1743127E-1, 3.7763609E-2, 2.7285441E+1, 2.7285656E+1
869   0.344 , 1.2156652E+0, 6.0731991E-1, 2.3083366E-2, 1.2156652E+0, 9.8736386E-2, 2.7285987E+1, -2.1743127E-1, 9.8240722E-2, 2.7285441E+1, 2.7285987E+1
870   0.703 , 1.1820003E+0, 6.0731991E-1, 2.3083366E-2, 1.1820003E+0, 1.5807049E-1, 2.7286316E+1, -2.1743127E-1, 1.5774994E-1, 2.7285441E+1, 2.7286316E+1
          ⋮
```

Attached document 7: “Sample of a kinetic data file (BELSORP MAX II / G / X - .NRAT)”

Record number

```
  1   ====================
  2   Instrument information
  3   ====================
  4   Instrument name    BELSORP MAX G
  5   Instrument S/N     001
  6   Software version   Version 1.1.1
  7   Vs_0(ml)   13.7121
  8   Vs_1(ml)   0
  9   ====================
 10   User information
 11   ====================
 12            ⋮
 13            ⋮
 14   ====================
 15   Adsorption kinetics measurement
 16   ====================
 17   time / sec  C           C0n         Cen         Pvsin       PVst        Pvdt        Vs          Vd          dvd
      Pvdt Thermal Yes        Vd-Non ideality No      Vd-Non ideality Yes     Vs-Non ideality No      Vs-Non ideality Yes

 18   0.219       4.12370E+0  2.00591E+0  1.66612E+0  4.14510E+0  4.12370E+0  4.12370E+0  1.37121E+1  1.46240E+1  0.00000E+0
      4.1237E+0               1.4623E+1               1.46240E+1
      6.7012E+0   1.91997E+4  4.12370E+3  3.04047E+2  0.00000E+0  4.14510E+0  0.00000E+0  1.46230E+1  0.00000E+0  7.01909E+0
      1.9199E+4   1.54125E-2  3.04047E+2  0.00000E+0

 19   0.281       3.95789E+0  2.00591E+0  1.66612E+0  4.14510E+0  3.95789E+0  3.95789E+0  1.37121E+1  1.46240E+1  0.00000E+0
      3.9578E+0               1.46230E+1              1.46240E+1
      6.2721E+0   1.91998E+4  3.95789E+3  3.04047E+2  0.00000E+0

 20   0.344       3.84248E+0  2.00591E+0  1.66612E+0  4.14510E+0  3.84248E+0  3.84248E+0  1.37121E+1  1.46239E+1  0.00000E+0
      3.8424E+0               1.46230E+1              1.46231E+1
      5.9702E+0   1.91999E+4  3.84248E+3  3.04047E+2  0.00000E+0

               ⋮

410   309.078     1.66605E+0  2.00591E+0  1.66612E+0  4.14510E+0  1.66605E+0  1.66605E+0  1.37121E+1  1.46234E+1  0.00000E+0
      1.6660E+0               1.46230E+1              1.46234E+1
      2.8504E+1   1.95086E+4  1.66605E+3  3.03885E+2  0.00000E+0

411   311.000     1.66612E+0  2.00591E+0  1.66612E+0  4.14510E+0  1.66612E+0  1.66612E+0  1.37121E+1  1.46234E+1  0.00000E+0
      1.6661E+0               1.46230E+1              1.46234E+1
      2.8759E+1   1.95110E+4  1.66612E+3  3.03885E+2  0.00000E+0

412   -999        -999

413   1.6660E+0   1.1111      1.66608E+0  1.66608E+0

414   0.203       4.50921E+0  3.04718E+0  2.80324E+0  4.52003E+0  4.50921E+0  4.50921E+0  1.37121E+1  1.46241E+1  0.00000E+0
      4.5092E+0               1.46230E+1              1.46241E+1
      2.8822E+1   1.95495E+4  4.50923E+3  3.03864E+2  0.00000E+0  4.52003E+0  1.66608E+0  1.46230E+1  0.00000E+0  2.95061E+1
      1.9549E+4   1.31469E+1  3.03864E+2  0.00000E+0

415   0.266       4.39461E+0  3.04718E+0  2.80324E+0  4.52003E+0  4.39461E+0  4.39461E+0  1.37121E+1  1.46241E+1  0.00000E+0
      4.3946E+0               1.46230E+1              1.46241E+1
      2.8775E+1   1.95495E+4  4.39461E+3  3.03864E+2  0.00000E+0

               ⋮
```

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