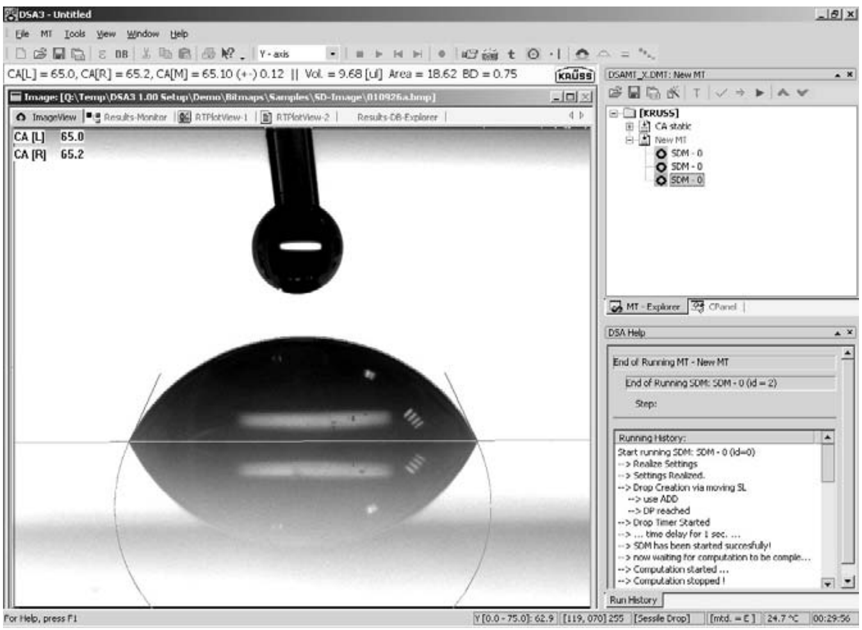
Software for Drop Shape Analysis



Installation and Operation

Manual

V1.72-02

Contents

Dear KRÜSS Customer,

Thank you for deciding to acquire a DSA100 Contact Angle Measuring System with the DSA3 software. With the DSA3 you will find yourself with the most up-to-date optical system for measuring surface tension and energy. DSA3 is, so to speak, the brain of the DSA100 – it controls the movements of the dosing unit, the axes and the optics – all of which can be automated as required – it records the measured data and permits its scientific evaluation, and it concludes the investigation with an exact measurement report.

This manual provides you with a step-by-step introduction to the software, it describes the whole range of functions and shows you how to use the software optimally. The manual is rounded off with an introduction to the theory of surface science.

Info about the DSA100 can be found in the instrument manual

This manual is subjected to continual quality control. You can download the current manual version at any time from the download region of our homepage www.kruss.de. You should also contact us if you have any technical questions about the DSA3 software or DSA100 and its components:

Update your manual via the Internet!

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Your possibilities with the DSA3 software

Together with the DSA100 Contact Angle Measuring System, the DSA3 software provides you with the following possibilities:

The available applications depend on the DSA100 version and the DSA3 components acquired.

If you want to extend your range of possibilities we will be pleased to advise you!

- Static and dynamic contact angle measurements on liquids drops in a gaseous or liquid phase
- Measurement of the surface tension of a pendant drop in a gaseous or liquid phase
- Calculation of the surface energy of a solid using a wide variety of models
- Evaluation of digitized drop images by various methods
- Automation of a complete measuring procedure with several liquids: volume dosing - positioning on the sample – setting the optics – contact angle measurement
- Automatic positioning with the help of a virtual sample and measurement of position related contact angles („Mapping“)
- Drawing up standard measurement templates (MTs) simply by using the MT-Wizard
- Measurements at high and low temperatures and with controlled humidity.
- Integral and extendable databases with substance data on liquids that can be linked directly to measuring data
- Comfortable data management
- Measurement reports with predefined or self drawn-up design

How to use this manual

This manual has been designed to guide you step by step through the DSA3 software and to familiarize you with all its possibilities.

Please do not forget the side notes: they frequently contain important information, offer keyword-type summaries and help you to decide whether a particular section is at all relevant for your own measuring system and your problems.

A look at the side notes is always worthwhile!

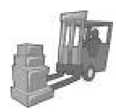
The DSA100 is a modular measuring instrument and allows all automation stages from mainly manual operation up to almost complete automatic control of the measuring procedure with the DSA3. As it is not possible to produce an individual manual for each individual hardware configuration, this manual contains all the software functions, even though some of them may not be required at all for your system.

A glance at the top page margin will help you with the orientation: the symbols used here show whether a motorized DSA100 component is required for a program function. If you do not have this component then simply skip the particular page. If only one section is affected then the symbol applies until the next heading on the page.

Info applying to particular DSA100 components can be recognized by the following symbols in the margins:

DSA3-controlled **dosing system** (simple or multiple). If you are only equipped for manual dosing then skip this section until the next heading.

DSA3-controlled **sample table/axes**. If you are only equipped with manual axes then skip this section until the next heading.



DSA3-controlled **optics**. If you are only equipped with manual camera zoom and camera focus (image sharpness) settings then skip this section until the next heading. However, the illumination is controlled by DSA3 in all configurations.

1 Installation

Software already installed? Then jump to page14.

It is possible that the software has already been installed if you have acquired your computer from KRÜSS GmbH or if the system has been installed by a KRÜSS technician. In this case you can skip this section.

Before the DSA3 installation the framegrabber board must have been built in and the driver installed. For an IEEE-1394 camera, the driver must also be installed (→ manual for the instrument).

Some functions of DSA3 do not work if no printer driver is installed. If no printer is connected to the computer, install any driver, for example a pdf printer driver.

Before the installation please read the “release notes” on the DSA3 CD. They may contain important information that is not yet covered in this manual.

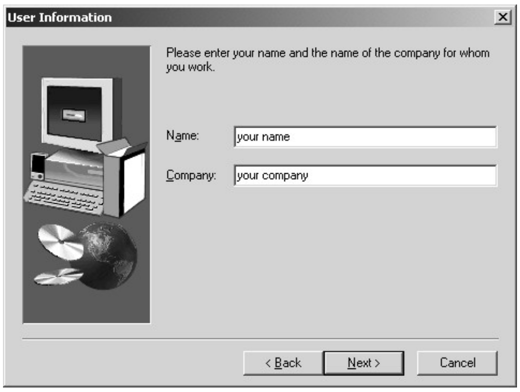
1.1 Main program

First close down all applications. Then insert the DSA3 CD-ROM in a CD-ROM drive. If the Windows autostart function is active the installation starts automatically. Otherwise, run the file “Setup.exe” in the “DSAsetup” folder. A Wizard will guide you through the procedure. “Next” will always lead you to the next step; you can use “Back” to return to the previous item.

Step 1: Welcome window and copyright information.

Step 2: Information concerning the version.

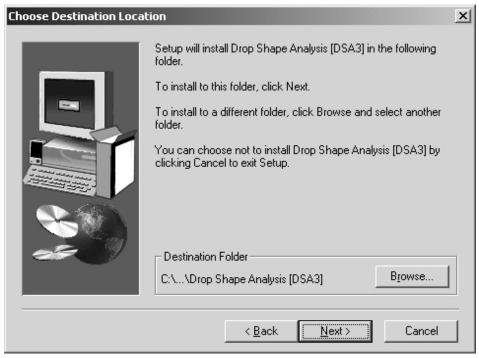
Step 3: Confirmation of the license conditions. You can only continue if you accept the license conditions with “Yes”.



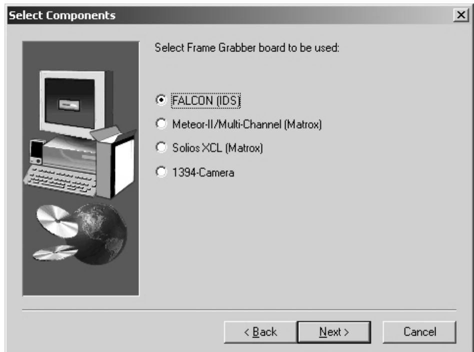
Step 4: Enter your user name under “Name” and your company name under “Company”.

Step 5: The registration data is shown again for checking. Confirm with "Yes" or correct the entry with "No".

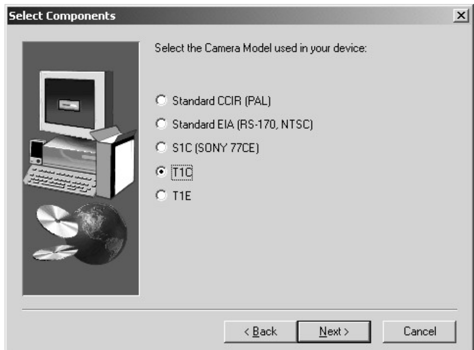
Step 6: Confirm the proposed installation directory with „Next" (recommended) or choose a different directory using „Browse".



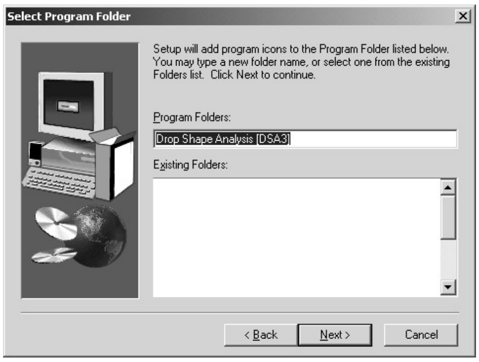
Schritt 7a: Selection of the installed framegrabber respectively IEEE1394 camera.



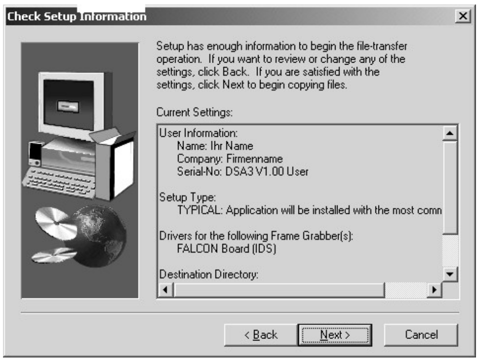
Step 7b: Selection of the camera type. This step is only necessary if the Falcon Framegrabber was selected.
The standard camera type is "T1C". This setting should only be changed if you use a camera that you have not obtained from KRÜSS.



Step 8: We recommend selecting the option "Typical" for the installation extent.
If insufficient memory space is available on the hard disk you can reduce the extent of the installation by selecting "Compact"; only those components that are absolutely necessary will be installed. Under "Custom" you can individually select the components you wish to install by placing ticks in the checkboxes.



Step 9: Enter the name of the program folder as it is to appear in the Windows start menu.
The recommended folder name is:
Drop Shape Analysis [DSA3]



Step 10: Check all the listed registration data and then close the installation with "OK". The necessary files will be copied.

Step 11: The computer must be restarted before the program start. If this is not to take place automatically at the end of the installation then select the option "No, I will restart my computer later."
The installation is terminated with "Finish".

Step 12: The mini CD delivered with the DSA CD contains the product key file „DSASP.DAT". Copy this file into the DSA3 folder which was created during the preceding installation process.

☝ DSA3 cannot be operated without the product key!

1.2 DSA Mapping Editor

The "DSA Mapping Editor" is a supplementary software for placing virtual drops on a virtual sample („Map"). The drop positions are transferred to DSA3 where they are used for dosing drops on an actual sample. The set-up program "setup.exe" is located on the DSA3 CD-ROM in the folder „DSAMAPED". During the run of the set-up only a program folder and a folder in the Windows start menu must be selected respectively confirmed.

1.3 Deinstallation

In order to uninstall the DSA3 software select the menu item "Settings"→ "System control". Open "Software" and select the DSA3 software from the list of programs shown. Select the function "Remove" and confirm the deinstallation in the following dialog.

For the „DSA Mapping Editor", an uninstall program is located in the Windows start menu.

2 Introduction to the software

2.1 General information about program operation

DSA3 is designed according to the operating guidelines of usual Windows programs. In this manual we have assumed that you already have the basic knowledge for working under Windows, such as use of the mouse or how to use menus. However, you can find much useful information in the Windows Help:

Many functions can only be found in the context menus (right-hand mouse key).

Context menus

The DSA3 software provides you with a wide range of program functions. In order that the main menu does not become a labyrinth we have assigned many functions to the so-called "context menus". A context menu is opened with the right-hand mouse key – it contains all the important menu entries that are required in connection with the particular screen element that has been clicked on.

Keyboard control

Use keyboard commands for controlling the DSA100!

Keys and key combinations are available for controlling motorized DSA100 components in particular. This means that you can avoid clicking backward and forward between control panels. A list of key commands is given on page 17.

2.2 Program start

Switch on the DSA100 first, then start DSA3.

And:

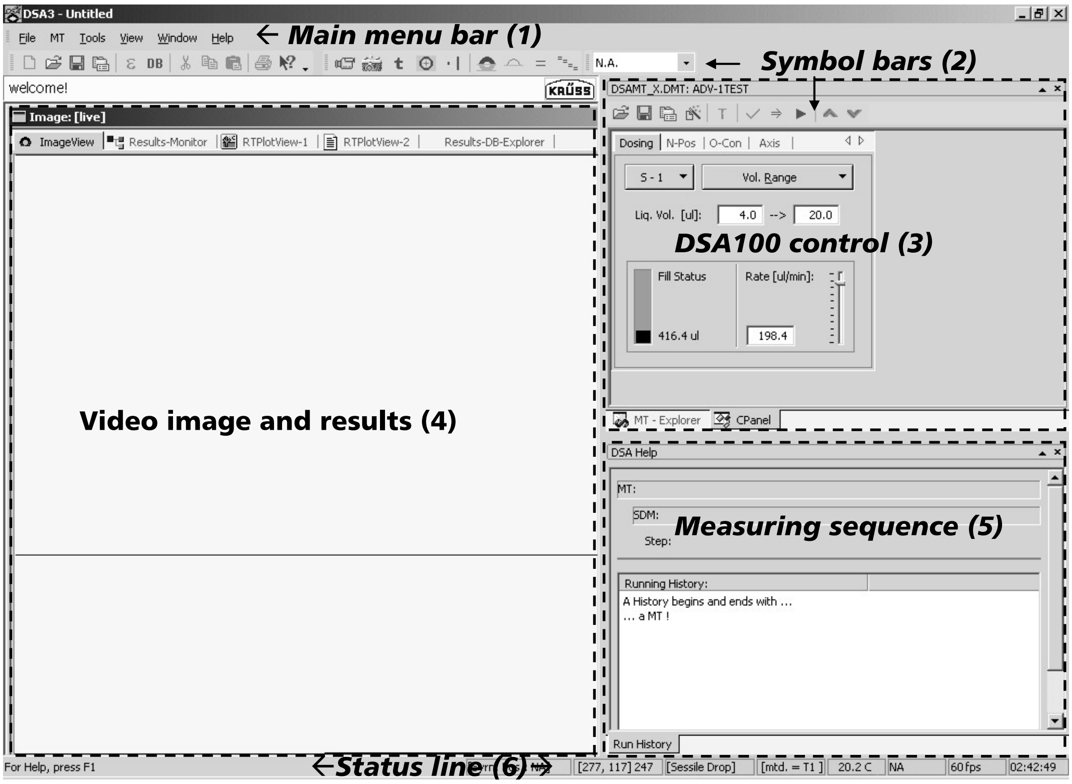
First exit DSA3, then switch off DSA100.

Before the program start the DSA100 must be connected up and switched on (→ DSA100 Manual). Some program functions are only accessible when the corresponding device components are available.

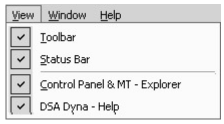
Double-click on the desktop icon

or select "Drop Shape Analysis" in the Windows start menu.

2.3 The program desktop



With "View" desktop elements can be hidden or displayed.



The appearance of the desktop depends on the settings with which the program was last exited.

Main menu bar (1)	Many of the DSA3 functions can be accessed via this menu. The context menus are also required.
Symbol bar (2)	By clicking on the icons in the symbol bar you can call up many program functions directly. A list of commands can be found in the annex (→p 19).
DSA100 control (3)	The control panel ("CPanel") for the direct control of motorized DSA100 components and the MT Explorer for drawing up and managing programmed measuring sequences
Video image and evaluation (4)	As well as the video image you will find the results of the current measurement here ("Results-Monitor") and their graphical presentation ("RTPlotView-1/-2"). You can manage an open results database under "Results-DB-Explorer".
Measuring sequence (5)	Sequential protocol of a started MT.
Status line (6)	Current measured values, shows the mouse position in the video image, information about the measuring mode, etc.

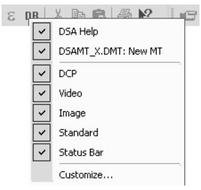
Cpanel *= "Control Panel"; DSA100 control field*

MT *= "Measurement template"; programmed measuring procedure*

2.4 Command icons

The command icons are located in the main menu bar and in a menu bar above the CPanel.

Menu bar and symbol display can be changed from of the context menu of the symbol line.



Main menu line	
Icon	***Function***
	Opens a file of the current window type.
	Saves the contents of the active window.
	Opens the settings menu for the current MT.
DB	Opens the substance database (liquids, solids, gases).
	Switches between live image and snapshot.
	Generates a snapshot for saving.
t	Resets a timer to 0 while a measurement is taking place.
	Determines the magnification factor (pixels/mm).
	Automatic baseline determination.
	Determines the drop shape according to the currently set analysis method.
=	Single measurement on the image with the method set in image window.
=‗=‗	Measurement series carried out according to the settings in the current current SDM, or start of a video recording, depending on the SDM's settings.

CPanel / MT-Explorer menu line	
	Opens an MT-Database.
	Stores the current MTs
	Opens the settings menu for the current MT.
	Opens the MT-Wizards (programming tool for MTs).
T	Transfers the current settings from the CPanel to the current SDM
	Sets the MT selected in the MT explorer as current MT.
	Drives all components to the positions set in the current SDM.
	Starts the current MT (=carries out an automated measurement).
	Liquid dosing according to the settings in the CPanel.
	Dosing in reverse direction („aspirate“).

2.5 Keyboard control of the DSA100

Illumination and all movable components of the DSA100 can be controlled directly via the keyboard.

To switch between the components to be controlled the <ctrl> key is used simultaneously with certain letters. The upper menu line shows the item currently under key control.

Control itself is (in most cases) carried out with <ctrl> and the keys <pg↑> and <page↓>

Illumination

The illumination is software controlled even with a fully manual equipment:

The illumination is changed in single steps. Press the key as often as necessary!

<ctrl> + „**i**":switching to illumination control

<ctrl> + <pg↑> bright <ctrl> + <pg↓> dark

List of keys

the key for the z-axis is <ctrl> "v" (vertical)

component	***switch***	***control***
x-axis	<ctrl> + **x**	<ctrl> + <pg↑>: right <pg↓>:left
y-axis	<ctrl> + **y**	<ctrl> + <pg↑>: back <pg↓>: front
z-axis	<ctrl> + **v**	<ctrl> + <pg↑>: up <pg↓>: down
syringe	<ctrl> + **s**	<ctrl> + <pg↑>: up <pg↓>: down ←: left →: right
illumination	<ctrl> + **i**	<ctrl> + <pg↑>: bright <pg↓>: dark
zoom	<ctrl> + **z**	<ctrl> + <pg↑>: large <pg↓>: small
focus	<ctrl> + **f**	<ctrl> + <pg↑>: high <pg↓>: low

2.6 Basic principles: measurements with templates (MTs)

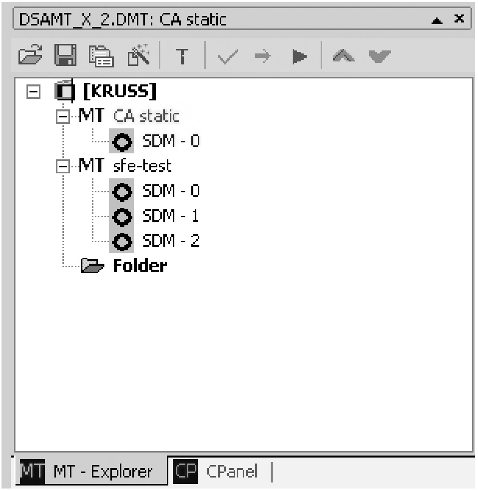
***Working sequence**:*
program MT → start MT or measurement series → transfer results to database → evaluate → generate measurement report

The basic principle behind working with the DSA3 is the use of predefined measuring sequences, the measurement templates, **MTs**.

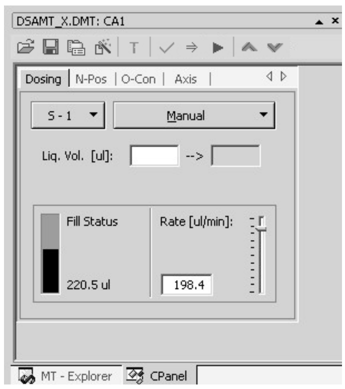
The MTs are displayed and managed in the MT-Explorer. With a fully equipped DSA100 a complete measurement on several different drops can be carried out fully automatically.
An MT contains one or more measurements on single drops - "Single Drop Measurements" **(SDMs)**.
The MT-Wizard helps with programming an MT; it can be opened via the icon.

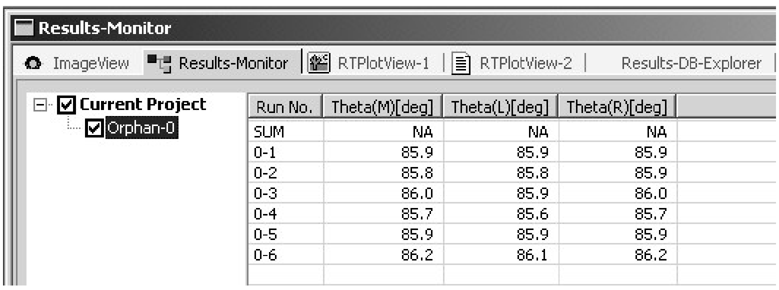
__SDM__ ="Single Drop Measurement"

The MT-Wizard is a useful tool for programming an MT



The "Control Panel" (CPanel) is used to help with MT programming. All moving components are controlled with its help. The set positions and dosing options can be assigned to the current SDM with the T button. When an MT has been fully programmed it can be started with the ▶ button.
Previously stored images can be analysed using the parameters of the current SDM with the button. If the SDM is programmed for a video recording, clicking on will start the recording.





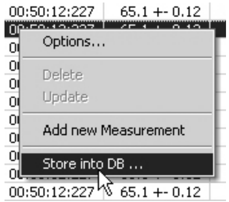
Run No.	Theta(M)[deg]	Theta(L)[deg]	Theta(R)[deg]
SUM	NA	NA	NA
0-1	85.9	85.9	85.9
0-2	85.8	85.8	85.9
0-3	86.0	85.9	86.0
0-4	85.7	85.6	85.7
0-5	85.9	85.9	85.9
0-6	86.2	86.1	86.2

The results obtained by processing an MT are first shown on the Results-Monitor. The data can be examined there and in the two plot windows "RTPlotView-1" and "RTPlotView-2".

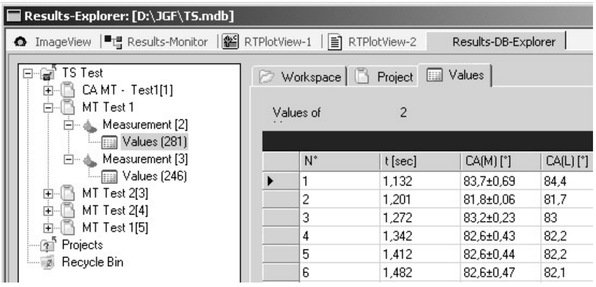
2.7 Data management and processing: the “Results-DB”

From the Results-Monitor the data is copied into the results database (“Results-DB”).

Raw data is copied into the database via the context menu of the Results-Explorer.



In “Results-DB-Explorer” the complete management and evaluation of the measured data is carried out. The database structure is as follows:



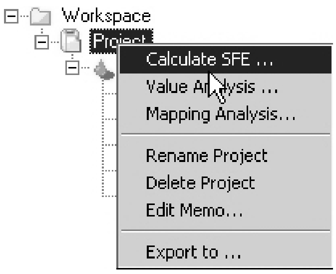
Workspace
- Project
  - Measurement
    - Values

Each of these hierarchy elements can be viewed and edited in “Results-DB-Explorer”.

Creating a new Results Database: context menu item “New DB”

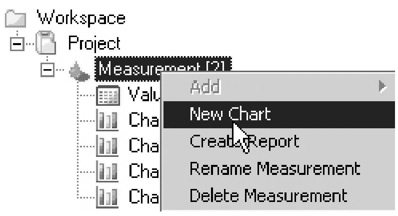
From the Results-DB-Explorer the following actions are also possible:

1. Evaluation of measurements from the context menu of a project. The **surface free energy** of a solid can be calculated from contact angle data (“Calculte SFE”). Average values can be calculated for all contact angles of the same liquid (“Value Analysis”). Data obtained using the mapping tool can be evaluated with “Mapping Analysis”.

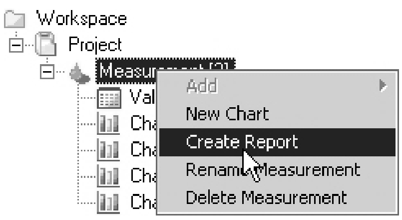


For calculating the surface free energy we recommend to select a corresponding MT template in the MT wizard.

2. A **graphical plot** of a measurement can be generated (context menu of a measurement).



3. A comprehensive **measurement report** can be produced (context menu of a measurement).



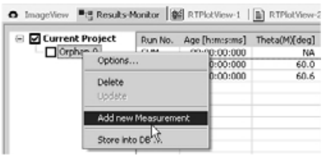
3 Measurements without running an MT

This section deals with measurements without using an MT. It also helps you to familiarise yourself with the two basic methods of DSA3 (contact angle measurement and measurement of the surface tension using pendant drops).

There are two possible ways to carry out measurements from the video image without running a programmed MT:

The single measurement is only used for test measurements. We recommend using an MT for regular measurements

1. = Carrying out a single measurement (live image or snapshot) outside an MT with selected parameters. If this is unwanted an new measurement series can be created in the Results-Monitor („Add new Measurement" in the context menu of the measurement series).

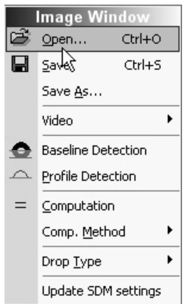


Video evaluation with the icon C

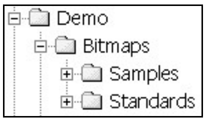
(→ p. 60).

2. Carrying out a series measurement (only live video). In this case the settings (method, statistics parameters, etc.) of the active SDM are used. A new measurement series is automatically created in the Results-Monitor.

3.1 Single Measurements (using demo images)



First insert the DSA3-CD. Now activate the image window in DSA3 and select the command "Open..." in the context menu. On the CD open the folder "Demo/Bitmaps/ Samples".




010926a.bmp

For a *contact angle* demo measurement select the folder „SD-Image" and open the file *010926a.bmp*.


yl_pd_50.bmp

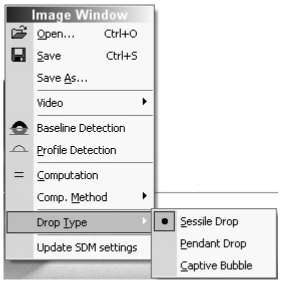
For a *surface tension* demo measurement select the folder *Standards/Pulsar or Falcon/* and open the file *yl_pd_50.bmp*.

3.1.1 Single measurement of a contact angle

For single measurements of contact angles all necessary options are located in the context menu of the drop image; some basic functions are also located in the symbol bar. First open the context menu.

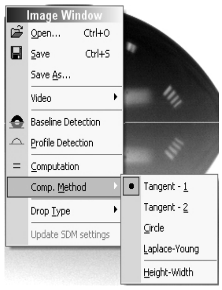
Selecting the drop type

Select the drop type under "Drop Type". As the demo image is that of a drop on a solid "Sessile Drop" must be selected.



Selecting the evaluation method

For "Sessile Drop" and "Captive Bubble" there are five different evaluation methods, whose meaning and use will be explained later (→p. 64 and 135). For this example select "Ellipse".



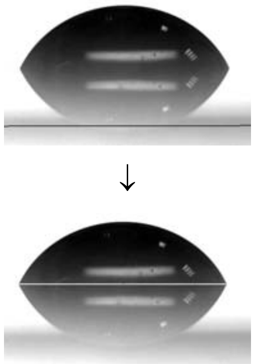
"Captive Bubble":

Air bubble in a liquid that is trapped beneath a solid.

The method "Ellipse" is also known as "Tangent method 1"

Determining the baseline

The baseline is the border at the point of contact between the liquid and the solid. Click on the button or select "Baseline Detection" in the context menu in order to determine the baseline in the image.



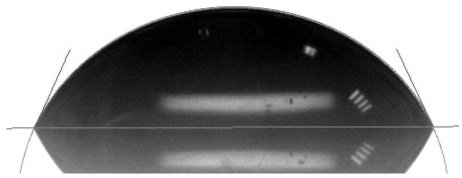
☝ For non-reflecting samples and contact angles above 90° corresponding settings must me made in the active SDM (→ p. 65)

Determining the profile

The drop profile is also determined from the image data. Click on the button or select "Profile Detection" in the context menu. The profile appears as a red line around the drop.

Carry out the CA measurement

When the settings have been made the single measurement is carried out with the = button or the context menu command “Computation”. A second green line appears around the drop; this is the mathematically calculated profile.

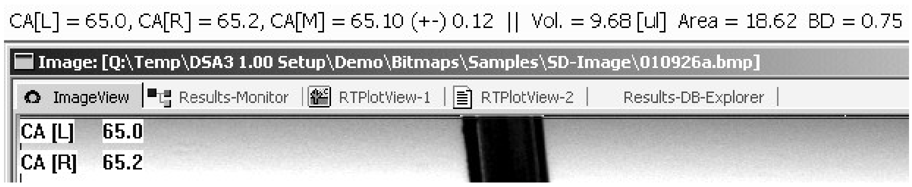


The quality of the measurement can be estimated by comparing the agreement between the blue and the green lines.

The tangents from which the contact angles are obtained also appear as red lines.

Result

The measured contact angle is shown at the top left of the framegrabber image. The complete results of the measurement are shown in the information line above the window:



The result is also transferred to the Results-Monitor. If no measurement has previously been made the measurement will be called “Orphan”, because it is not assigned to an MT.

3.1.2 Single measurement of the surface tension (SFT)

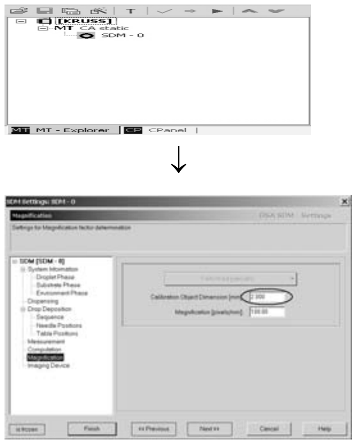
The example shown in this section uses the demo image „yl_pd_50.bmp“ (→ p. 20). The commands for the single measurement can be found in the context menu of the drop image; some basic functions are located on the symbol bar.

Defining the needle diameter

A micrometer screw for measuring the needle diameter is part of the DSA100 supply.

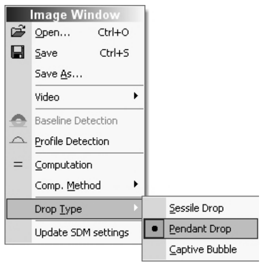
In contrast to contact angle measurements, the absolute size of the drop must be known for measuring the surface tension. Before the measurement the magnification of the image is determined using the width of the needle as the reference. The diameter of the special needle used for SFT measurements must therefore be determined.

When carrying out real measurements, a special MT is to be created for the SFT measurement. However, for this introduction you can also select the current MT "CA Static" which appears when the program is started; this is originally intended for contact angles. Click on "SDM-0" with the right-hand mouse button and select the menu item "Settings".
In the menu bar select the left-hand option "Magnification" and enter the diameter of the needle under "Calibration Object Dimension"



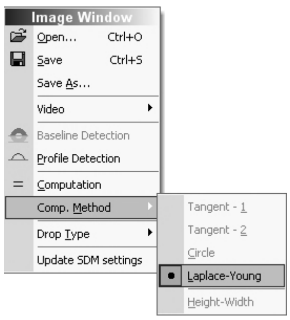
Selecting the drop type

Surface tension is measured on pendant drops. Select this type under the menu item "Drop Type".



Evaluation method: Young-Laplace

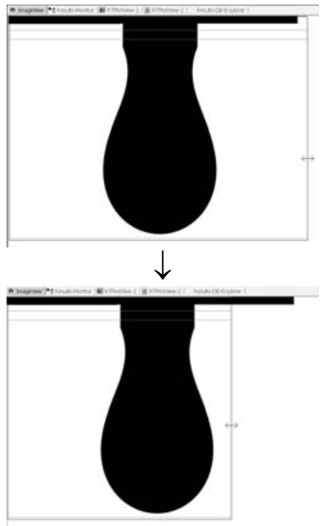
Pendant drop measurements are only possible with the Young-Laplace method. The other evaluation methods are therefore inactive when drop type "pendant drop" has been selected.



Evaluation range (Region of Interest)

When the evaluation range corresponds to the whole image the frame cannot initially be seen. This means that to move the line you should click on the image margin (<Shift>+mouse-click).

If - after moving the line - multiple lines can be seen then just bring a different window into the foreground and then change back to the Image-View window.



The image of the pendant drop is outlined by blue lines. Four further blue measuring lines can also be seen in the image.

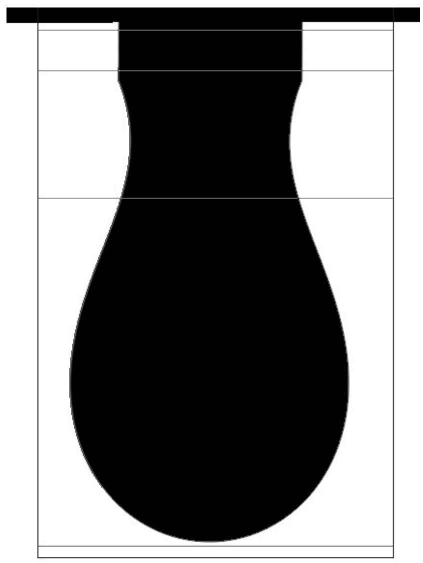
The frames define that part of the image that is actually to be evaluated ("Region of Interest"). The closer this region is drawn around the drop image, the shorter the calculation time required. This region can be altered by clicking on one of the outer limit lines with the <Shift> key pressed down and moving it with the mouse.

Due to possible disturbances at the edges we recommend a size reduction of at least a few pixels at each side.

Setting the measuring lines

The identical procedure is carried out with the live image in a "real" measurement.

Some lines may also be located at the upper margin of the image, so that it may not be possible to see all the lines initially.



Three of the four horizontal measuring lines must be positioned with the mouse (click on them and move them). The two upper measuring lines are positioned so that they include part of the needle tip in the image. In this part of the image the known needle diameter is used to determine the image magnification. The third line is positioned below the contact line between needle and drop. The drop shape will only be determined below this line; in this way the region of the drop that is distorted by the needle contact can be excluded from the calculation.

The fourth line is used for contact angle measurements and is irrelevant for SFT. It can be placed beneath the drop image.

Determining the magnification of the image

To determine the magnification click on the icon . The magnification is then shown together with the reference diameter in the Info line above the “ImageView” window..

During a measurement on a live image the magnification must be redetermined each time that the camera zoom and focus settings are altered!

When measuring SFT using an MT, the measured magnification must be transferred to the current SDM with the transfer button .

Determining the shape

The drop shape is determined from image data. Click on the button or select “Profile Detection” in the context menu. The contour line appears as a red outline around the drop.

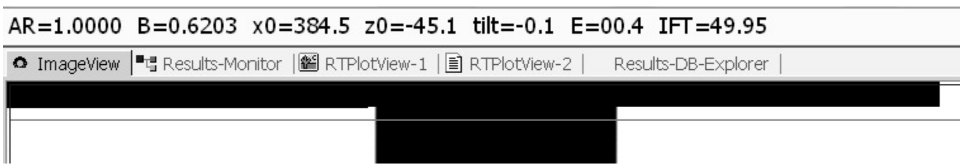
Carrying out the surface tension measurement

The single measurement is carried out with the defined settings by using the button or the context menu command “Computation”. A second green outline appears around the drop; this describes the mathematically calculated contour.

You can estimate the quality of the measurement from the degree of coincidence between the red and the green lines.

Result

The measured data is shown in the info line:



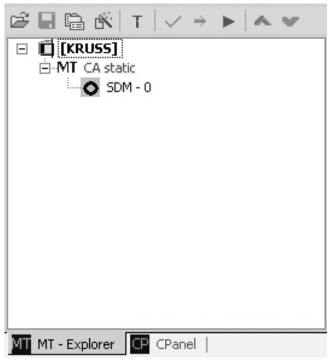
In addition the result is transferred to the Results Monitor. If no measurement has previously been made the measurement will be called “Orphan”, because it is not assigned to an MT.

3.2 Series measurements

A series measurement always refers to the settings (timing, measuring method, image scale) in the current SDM of the current MT.

More details about using and programming MTs is given at →p.41 ff.

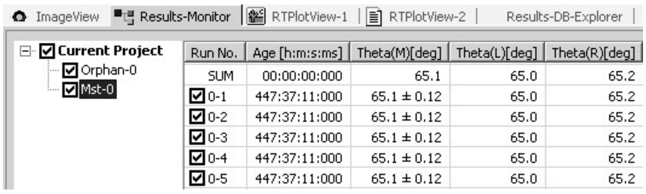
After the first start of DSA3 there is already an MT with an SDM in the MT-Explorer. Select the MT "CA static" and click on the button to define it as the active MT. If several SDMs are present then you can also select an SDM for activation. All series measurements refer to the active SDM. The menu settings for the single measurement (→Chapter 3.1.1) are not used.



Carrying out the series measurement/Result

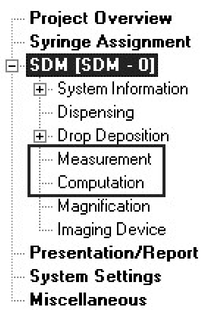
Dose a drop of water on a highly reflective sample and obtain a sharp image of the drop in the "Image View" window.

All the operating steps that you carried out in sequence for the single measurement are now carried out automatically. Click on the button. The series measurement will be carried out; it is finished after about 5 seconds. A new measuring series will be automatically generated in the "Results-Monitor".



Parameters

The measurement parameters can be viewed and edited in the MT-Explorer by selecting the active SDM and clicking on the button. The relevant parameters for sessile drop measurements can be found under "Measurement" and "Computation"; their use is explained on →pp. 59 and 64.



4 The Control Panel (CPanel)

The CPanel contains 4 tabs for controlling the motorized components: dosing system, axes (or wafer table or tilting table), camera optics and humidity chamber. If your system has no motorized DSA100 components then only the illumination can be controlled from the CPanel.

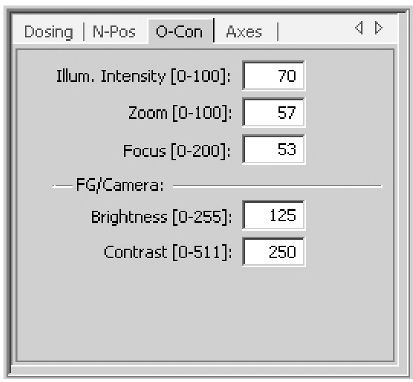
Before you start to use MTs, use the CPanel to familiarize yourself with the properties of the DSA100.

The CPanel carries out three important DSA3 functions:

1. Controls components of the DSA100. Complementary to the key control the illumination, the motor-driven components and the optional IEEE-1394 camera can be driven via the CPanel.
2. Helps with programming MTs by assigning positions and settings. Settings in CPanel can be transferred to the SDM by clicking on the T button.
3. Dosing for measurements not using an MT sequence.

4.1 Illumination

The intensity is controlled via the “O-Con” (Optic-control) tab. Click on the field alongside “Illum. Intensity” with the mouse. Enter either a numerical value between 0 (dark) and 100 (bright) or alter the value with the cursor keys ↑ and ↓.



Numerical entries must be confirmed with <Return>.

The values for “Brightness” and “Contrast” control the brightness and contrast for the framegrabber. You should only make alterations here if you cannot achieve a good image with the illumination settings.

For the optional IEEE 1394 camera, settings for the “Shutter” and the “Gain” must be made (→ pages 75f.)

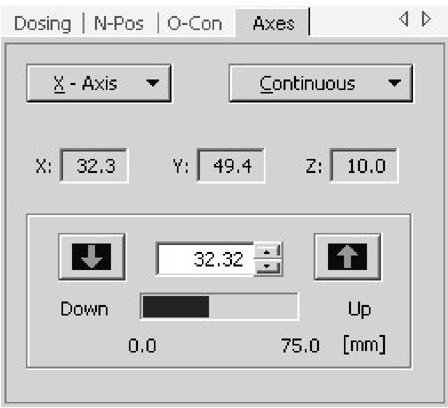
4.2 Sample table positioning

Before using the axes you must make sure that no objects are located within the range of movement of the axes or the vicinity of the guide rail. Keep your hands off the range of movement as otherwise injuries could occur.

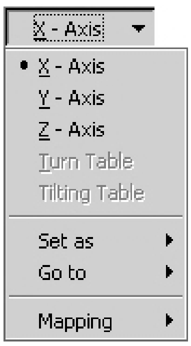
The x-position (left-right), the y-position (front-back) and the z-position (up-down) of the sample table are controlled via the "Axes" tab of the CPanel.

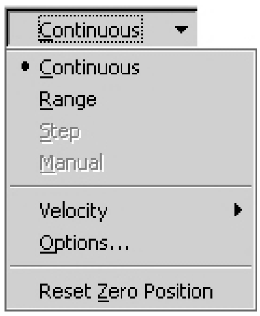
If the "Axes" tab is uppermost then the x-, y- and z-axes can be controlled directly via the keyboard.

Sample table direction	***Key***
To the right (x-coordinate increases)	PgUp ↑
To the left (x-coordinate decreases)	PgDn ↓
To the back (y-coordinate increases)	Cursor →
To the front (y-coordinate decreases)	Cursor ←
Upward (z-coordinate increases)	Cursor ↑
Downward (z-coordinate decreases)	Cursor ↓



In menu control the **left-hand** drop-down menu is used for selecting an axis and for storing standard sample table positions. All the axes and sample tables to be found will be shown there.
The **right-hand** drop-down menu is used for selecting the movement mode and contains some control options.





4.2.1 Stored axis positions

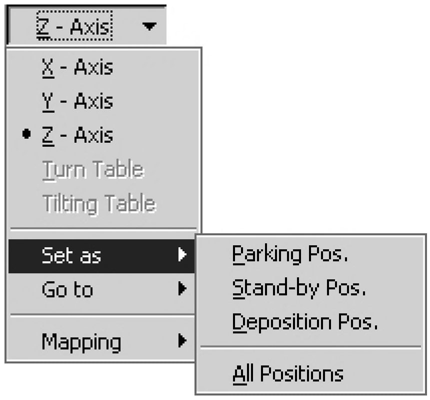
For automatic instrument control with an MT/SDM stored axis positions are used.

The following positions can be stored:

Parking Position: The basic position before and after a measurement.

Standby-Position: Table stand-by positions during a measuring sequence.

Deposition Position: The axis position for contact between drop and surface.



For a Mapping measurement, the set "Deposition Position" will be ignored. The drop positions on the sample refer to the mapping data and the "sample origin" which is set with the CPanel (→ 10.2.3).

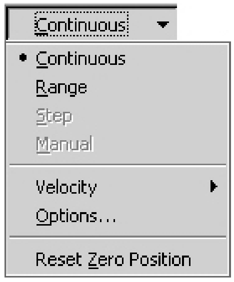
The position is not only saved for the currently selected axis, but also for all available axes. First move to the required position for *all* axes and then define it by using the menu item "Set as".

„Set as" stores the positions of all axes simultaneously!

- "All Positions" assigns the current axes settings to the 3 storable positions at the same time.
- With the function "Go to" you can move directly to the three stored positions.
- The stored positions can be used as often as required and only have to be redefined after each new start of DSA3.

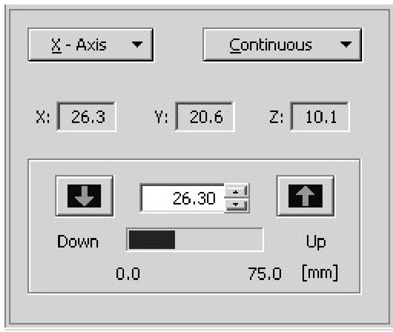
4.2.2 Axis movement modes

There are two movement modes for controlling the axes: “Continuous” and “Range”. The shown modes “Step” and “Manual” have not yet been implemented.
With “Reset Zero Position” the current axis is moved to its zero position.

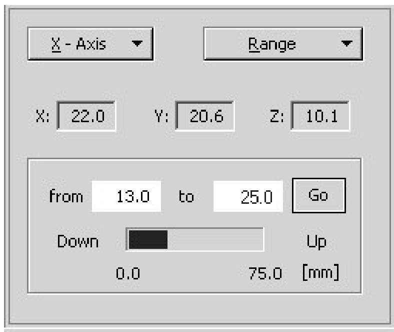


“Up” and “Down” refer to the alteration in the coordinates of the particular axis – not to an up or down movement.

Continuous: continuous movement until user termination or until endpoint is reached. The movement is started with the arrow keys “Up” and “Down” and stopped by clicking on the same button.
You can also enter a numerical value for the coordinate – this will then be moved to immediately that the <Return> key is pressed.

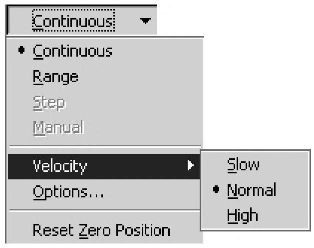


Range: moves the axis between two defined coordinates. The current axis will first move to the coordinate “from” and then to the second coordinate set under “to”. The movement is triggered with “Go” and cancelled with “Stop” (the button label changes).



4.2.3 Movement velocity

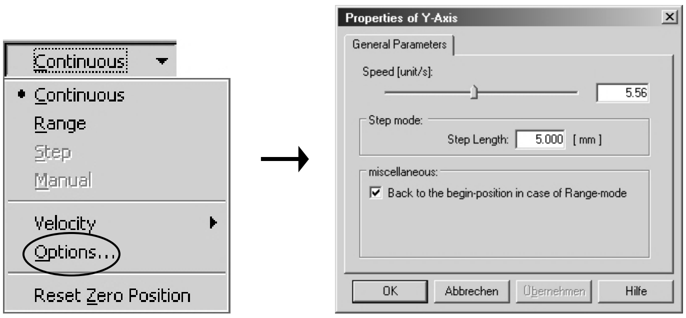
Three different speeds are available for the axis movements: "Slow", "Normal" and "High"; these can be selected for each axis separately. The velocity information in an MT also depends on these basic settings.



"Normal" is the standard velocity recommended for most cases.

The percentage values for the sequence in the MT settings are related to the velocity set here.

4.2.4 "Options"



The settings under "Step mode" are not yet effective.

Fine adjustment of the velocity

A fine adjustment of the axis' velocity can be carried out under "Speed".

This setting corresponds to the three speed stages (see above).

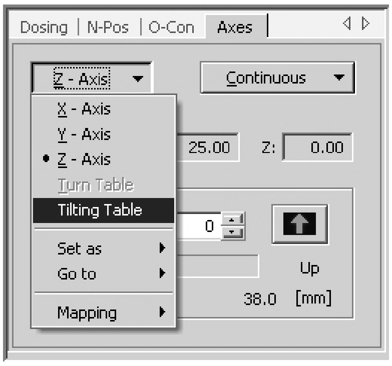
Driving back to the start position in the "Range" mode

When the option "Back to begin position in case of Range mode" is selected the concerning axis will drive back to the position set under "from" after the target position was reached.

4.2.5 Controlling a tilting table

When working with a tilting table, please follow the safety instructions in the DSA100 manual.

Select the tab sheet "Axes" in the CPanel. Select the option "Tilting Table" in the left drop-down menu.



Selecting the movement modes, controlling the table and setting the movement velocity is carried out the same way as for the axes (→ ch. 4.2.2 to 4.2.4). The range of movement is 0 to 90°.

☝ In contrast to the axes, the tilting table movement can't be programmed and embedded in an MT. If the tilting table shall be used during an MT run its movement must be controlled with the CPanel.

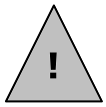
☝ The "Parking", "Stand-by" and "Deposition" positions are also not used for the tilting table.

Reset to initial position

To reset the tilting table to its initial position: select the menu item "Reset Zero Position" in the right drop-down menu.

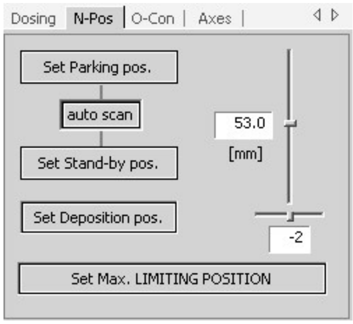
4.3 Needle positioning

Only move the needle behind the attached protection screen of the DSA100 (→ DSA100 Manual). Keep your hands off the range of movement of the needle. Otherwise they could be injured and, if toxic liquids are being used, poisoning could occur.



The height position of the needle and the offset to the left and right are controlled from the "N-Pos" tab of the CPanel.

The needle should be controlled either with the keyboard or by entering the co-ordinate (confirm with <Return>).
The slider indicates the current position. It can also be used to move the needle but is not suitable for fine adjustment.



With a "Single Direct Dosing" system only the height can be controlled!

If the "N-Pos" tab is active then the needle can be moved directly via the keyboard:

Needle movement	***Key***
down	Cursor ↓
up	Cursor ↑
to the left	Cursor ←
to the right	Cursor →

4.3.1 Automatic needle positioning ("auto scan")

If you click on the "auto scan" button then a search will be carried out automatically to get a good starting position for the needle at the very top in the centre of the image (see illustration on the right). The positions are automatically saved as Parking and Stand-by Position (→ sect. 4.3.2).
The search procedure can be cancelled by clicking on "auto scan" again.

Before using "auto scan " move the needle downward to check if the needle appears in the live image. Adjust the optics if necessary.

4.3.2 Stored needle positions

Stored needle positions are used for the automatic control of the needles during an MT sequence. As the suitable positions for making a measurement depend on the dimensions of the sample this means that the positions must be saved before an MT is started. The stored positions can be used as often as required and only have to be redefined when a new program is started.

The position is not only stored for the currently selected needle but for all available needles.

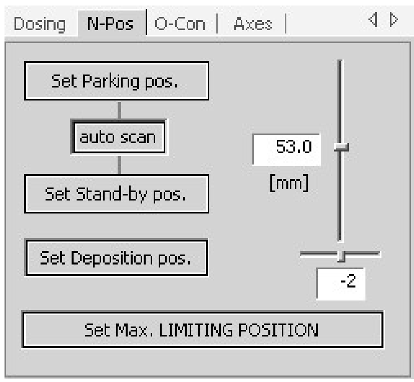
The use of stored needle positions for an MT is explained on page 54 and following.

Parking Position: the initial position of the needle before and after a measurement.

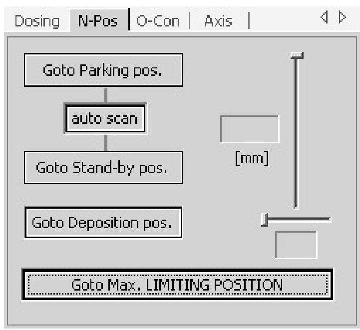
Stand-by Position: the stopping position of the needle during a measuring sequence.

Deposition Position: the needle position for the contact between drop and surface.

Max. Limiting Position: This function is used to define the current needle position as the lower limit for the needle which is not to be infringed when working with the "Auto Delivery" option (→p. 55).

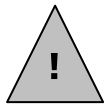


If you press down and hold the <Ctrl> key then the key marking "Set" will change to "Goto". You can then move directly to the stored positions by clicking on the corresponding buttons.

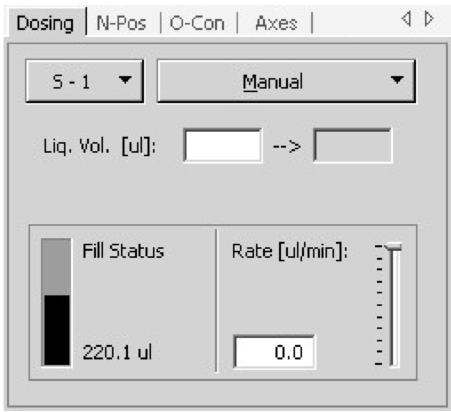


4.4 Syringe selection and dosing

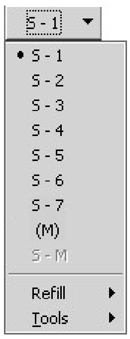
When a different syringe is selected the needle selector rotates. The needles should only be moved behind the attached protection shield of the DSA100 (→ DSA100 Manual). Keep your hands off the range of movement of the needle. Otherwise they could be injured and, if toxic liquids are being used, poisoning could occur.

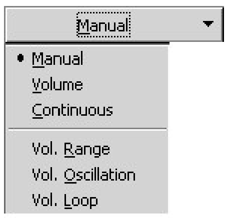


The choice of syringe and control of the dosing process outside an MT are made using the "Dosing" tab of the CPanel.



In menu control the **left-hand** drop-down menu is used for selecting a dosing syringe and for setting filling options. The number of syringes shown depends on your equipment level; a position marked with "(M)" stands for an additional manually operated syringe.
The **right-hand** drop-down menu is used for selecting the dosing mode. Outside an MT, the settings (dosing mode, volume) refer to all syringes.





The input fields below the menus are used for entering volume target values. If the right-hand field is grey then the entries there are irrelevant for the selected mode.

In the lower part of the tab the current filling level of the selected syringe is shown on the left. The dosing rate is set on the right-hand side. However, the CPanel will not "notice" an alteration in the rate if a syringe is exchanged. If the syringe is used for an MT then the rate can be stored there for each syringe separately.

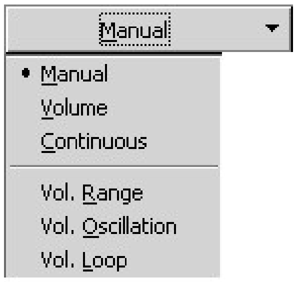
A good guide value is 100-150 µl/min. For more viscous liquids (e.g. glycerol) the rate should be reduced slightly.

If you want to carry out a dosing procedure outside an MT sequence, e.g. in order to find a suitable drop size, you should use the  buttons. The left-hand button starts dosing according to the currents settings. With the right-hand button you can reverse the dosing direction in the dosing modes "Manual" and "Continuous".

4.4.1 Dosing mode

Six dosing modes are available for controlling the dosing procedure; each syringe can be assigned an individual mode.

Manual: dosing takes place for as long as the button is pressed down. If this option is selected for an SDM then a dosing request will appear during a measuring sequence. The value entered in the left-hand field is irrelevant.



Volume: the exact volume entered in the left-hand input field will be transferred.

Dosing modes

Static:

Manual
Volume

Dynamic:

Manual
Continuous
Vol. Range

Hysterese:

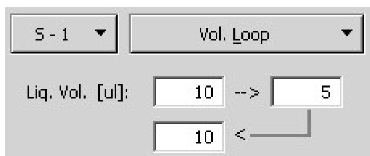
Oscillation
Loop

Continuous: dosing takes place by clicking on the button and only stops when the same button is pressed again.

Volume Range: a drop will first be generated with the volume entered on the left and then increased or reduced to the volume shown on the right.

Volume Oscillation: a drop will first be generated with the volume entered on the left. The drop size will then alternate continuously between the values entered at the right and left.

Volume Loop: a drop will first be generated with the volume entered on the left and then increased or reduced to the volume shown on the right. In a third step the drop will then be set to the volume entered at the bottom left.



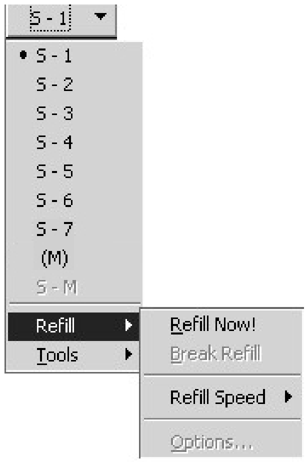
For the three last-mentioned modes, a certain speed can be defined for each Step (e.g. for "Range": fast dosing until the start volume is reached, then slow dosing until the final volume is reached).

More information about the use of the dosing modes in static or dynamic measurements is given on page → 53.

4.4.2 Refill options

With the "Refill" function in the left-hand drop-down menu the currently selected syringe is refilled. After it has been triggered the "Break" command becomes active; this can be used to cancel the started refilling process.

The slow "Refill speed" is only required for very viscous liquids.



4.4.3 Empty, rinse, reset syringe

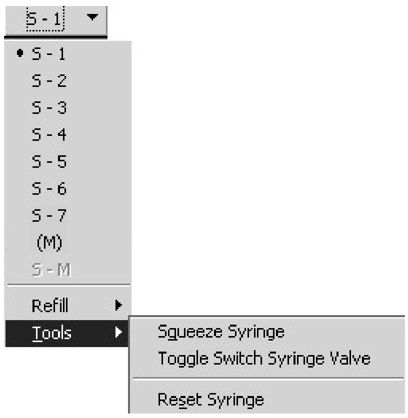
Under "Tools" you will find further options for controlling the current syringe.

Some "Tools" functions transport large volumes of liquid through the needle. Place a collection vessel below the needle.

Even on cancellation the current squeeze step (emptying or filling) will be carried out to the end!

The current syringe can be rinsed with the "Squeeze" command. The syringe will be continuously emptied and refilled until the squeeze process is terminated by pressing the <Esc> key.

"Toggle Switch Syringe Valve" switches the dosing valve in order to rinse the length of tubing between the storage bottle and the syringe. While dosing, the liquid will be transported not to the needle, but back into the storage bottle (or waste vessel). The switch has no effect on the squeeze mode.



With "Reset Syringe" the current syringe is initialized. As small volume errors become noticeable after some time which result in an incorrect filling level display, you should carry out this function from time to time.

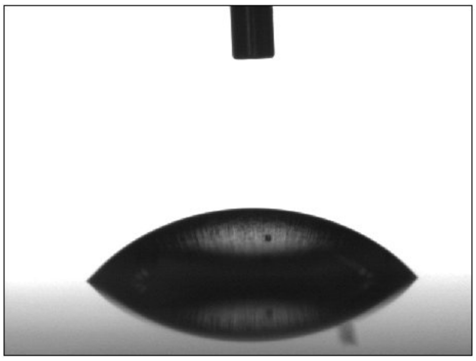
4.5 Setting the zoom and focus

Achieving a good drop image

If the background is too bright the drop shape will be outshone which leads to inaccurate measurements.

For very small contact angles (0-10°) use the manual DSA100 blind!

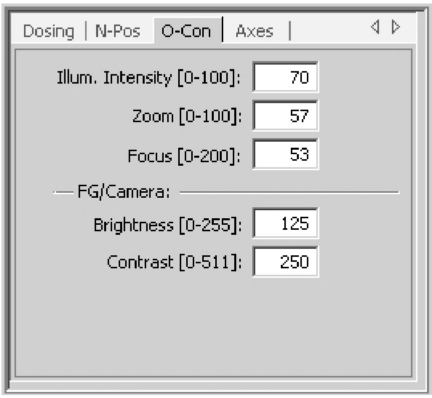
The drop to be measured should be large and should appear in the image as being as sharp and with not too bright a background. In dynamic measurements you must take care that even the largest extension of the drop is still shown completely in the image.
After the zoom and the focus have been altered it is generally also necessary to adjust the intensity.



Control of zoom and focus

In addition to controlling the illumination, the "O-Con" tab permits the motorized control of the zoom and focus.

This is done by clicking on the corresponding input field and altering the value, either with the cursor keys or by entering the numerical value directly.
You can also assign the zoom and focus to the current SDM with the T button.

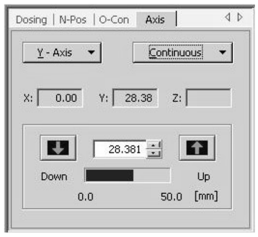


4.6 DSA100M (Micro): table positioning and dosing

The DSA100M comes with a special sample table PS3240 optional) and a piezo dosing unit.

Controlling the sample table PS3240

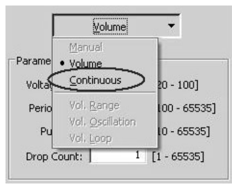
The micro-step sample table PS3240 contains an integrated x-axis and y-axis.



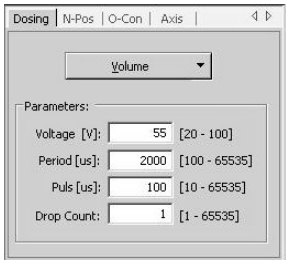
The axes are controlled in analogy to the standard axes with the difference that the range is limited to 50 mm but the position can be controlled exactly to 1 μm.

Controlling the piezo-dosing unit

To search for the dosing position in the image (→ DSA100M manual) it is helpful to set the dosing mode to "conti-nuous". The pro-duced permanent liquid stream is easier to find.



The piezo dosing unit for DSA100M is different from the standard dosing units. Only a relative drop size can be set for the resulting volume. Dispensing with a piezo-unit can be embedded in an MT and SDM.



"Voltage": The power of a single impulse results from the set voltage.

"Period [μs]": Sets the time for a single pulse

"Pulse [μs]": Sets the length of a single pulse.

"Drop count": Indicates how often the pulse sequence is repeated to form multiple drops.

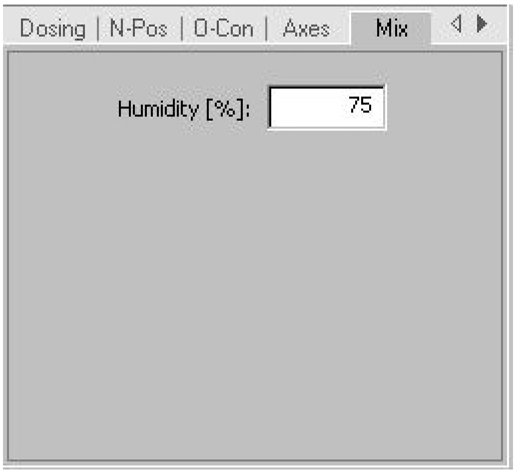
In the example shown, 20 pulses with 100 [μs] each are applied without repetition.

The volume actually produced is dependent on further factors as viscosity, temperature and individual properties of the micro pump; experience must be gained by the user. However, some helpful hints can be given:

- The manufacturer recommends a pulse width of 100 μs and a variation of the voltage between 50 and 70 V. The drop volume is mainly regulated by changing the period within a range of 1000 to 10000 μs.
- Higher viscosities require an increased voltage.
- To obtain small volumes, the pulse width can be reduced. However, it can then be necessary to raise the voltage.
- If no drop is produced a too low voltage can be the reason. If the drop splashes or sprays a too high voltage can be the reason.

4.7 Adjusting the humidity for HC10

If the Humidity Chamber HC10 is connected to the DSA100 properly an additional tab sheet named „Mix“ is added to the CPanel.



The required value for he humidity (in %) must be entered in the text box. The actual value measured by a humidity sensor inside the chamber is indicated in the status line.

Take care that the chamber is always filled with distilled water up to at least one third.
(→ DSA100 manual)

Wait with the measurement until the humidity inside the chamber has reached the desired value. It is normal if the measured value fluctuates around the desired value for a few percents.

In this state it is only possible to read out the temperature inside the chamber with the help of an external temperature sensor.

5 Using the MTs

The MTs are measuring sequences that must first be programmed (for programming → Section 6) and then only have to be started in order to make a measurement. An MT can be carried out as often as required. All the relevant measuring data is generated during the MT sequence and initially appears in the Results-Monitor, from where it can be transferred to the Results-Database.

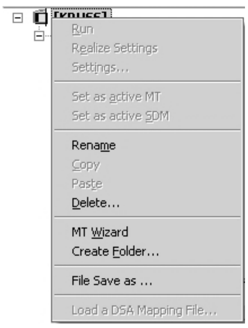
5.1 Management

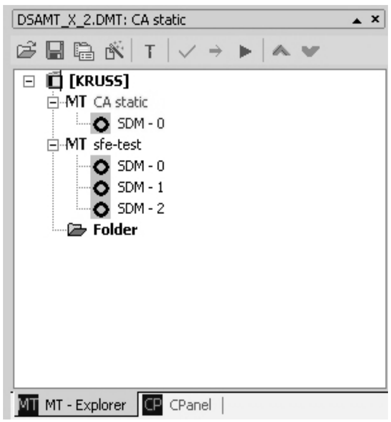
The MT-Explorer is used for the management of MTs. The first time that the program is opened you will find that it already contains a prepared folder structure with the file name "DSAMT_X.DMT" for various types of measurement with the DSA100. Each alteration is automatically saved in this "DMT" file ("DSA Measurement Templates") with the button above the MT-Explorer.

The button can be used to open a previously saved DMT file. At the start of the program the DMT file that was in use the last time that the program was exited will always appear.

Each MT is stored in a folder (or subfolder). SDMs belonging to an MT are hierarchically arranged within the MT.

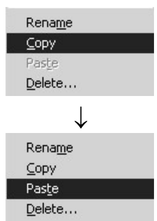
From the context menu of a folder you can generate a subfolder ("Create Folder"), rename the current folder ("Rename") or delete it ("Delete").





With <Ctrl> or from the context menu of an MT you can save the current "DMT"-file under a different name.

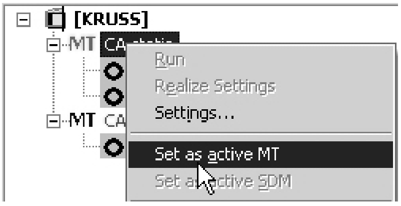
The commands "Rename" and "Delete" are also available in the context menu of an MT or SDM. Existing MTs or SDMs can also be copied into a different folder with "Copy" and "Paste" (context menu).

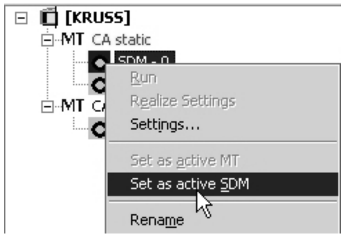


5.2 Processing MTs and SDMs

In order to process an MT you must first select it from the directory structure and then activate it. This is done via the context menu with the command “Set as active...”.

In the Explorer an active MT is shown in red, an active SDM in blue.





Alternatively the button can be used.

5.2.1 Start MT/SDM

An active MT or SDM is started with the button or via the context menu command “Run”. A single SDM can also be started separately from its context menu; in this case the other SDMs of the same MT will not be used.

Before the start you should make sure that

- You have selected the correct MT / SDM.
- That the current settings of the MT / SDM are still suitable for the actual situation (e.g. sample dimensions).

After the start either the selected MT with all its associated SDMs or only the selected SDM will run automatically. The procedure will be protocolled in the “History” (bottom right). If any manual steps are necessary during the measurement (e.g. manual dosing, manually moving to a new sample position) then the appropriate request will be displayed during the MT sequence.

5.2.2 Stop running MT/SDM

Cancel with <Esc>!

Measuring data recorded up to this point will be retained in the Results-Monitor.

When pressing <Esc> you will be asked whether the entire MT shall be aborted. By clicking on “No” only the currently running SDM will be aborted and the MT run will continue with the subsequent SDM.

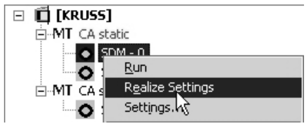
5.2.3 Adapting MT/SDM per teach-in (CPanel)

As the procedure of an MT often does not change and only positions need to be adjusted, you can use CPanel to “inform” the current SDM of the adjustments with the T button.

For example, if the height of the sample changes then you can adapt the required position for both the syringe and the axes, save the new Park, Stand-by and Deposition-Positions and transfer them to the current SDM with T. Except for the Refill and Tool functions for the syringes you can copy all the parameters from the CPanel into the active SDM, e.g. the dosing mode or optic settings, etc.

5.2.4 Implementing the MT settings (“Realize settings”)

With the context menu command “Realize Settings” or the ⇛ button you can also transfer parameters of the active SDM to the instrument and accordingly to the parameters of the CPanel.



*⇛ realizes parameters of the **active** SDM and not those of an SDM marked under Explorer!*

For example, if you have programmed a particular axis setting for an SDM you can move to it automatically with the “Realize” command – the new coordinates will also appear on the “Axis” tab.

5.2.5 Adapt MT manually

The parameters of an existing MT can be adapted via the command “Settings” in the context menu of an MT or via the button above the MT-Explorer

*opens the parameters of the **active** MT and not those of an MT marked under Explorer!*

Once an MT has been drawn up it can be modified as required. However, you must take care that any alterations made will be suitable for the selected measurement type. For example an MT designed for contact angle measurements should not be altered to a pendant drop MT.

6 Programming MTs: the MT-Wizard

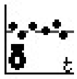
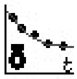
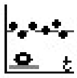
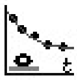
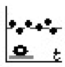
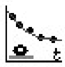
The MT-Wizard is opened with the button; it is used to program an MT step by step or by selective choice of menu. You should first select a template from it and then create the MT in the required MT folder.

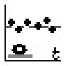
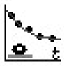
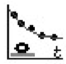
Information about the theory behind the measuring principles can be found in the Theory section 0.

***Pendant Drop**: Drop hanging from a needle.*

***Sessile Drop**: Drop lying on a solid surface. Measured using the thinner standard needle.*

MT-Types: An overview

MT Type	*Templates*	*Meaning*
γ SFT/IFT - Measurement Pendant Drop Method Sessile Drop Method	 SFT/IFT - static [PD]  SFT/IFT - dynamic [PD]	Measures the surface and interfacial tension (SFT/IFT) of a liquid on a pendant drop. **static**: time-independent measurement **dynamic**: measurement as a function of time
γ SFT/IFT - Measurement Pendant Drop Method Sessile Drop Method	 SFT/IFT - static [SD]  SFT/IFT - dynamic [SD]	Measures the surface and interfacial tension (SFT/IFT) of a liquid on a sessile drop. **static**: time-independent measurement **dynamic**: measurement as a function of time
θ Contact Angle - Measurement Using droplet of constant volume Using droplet of changing volume	 Contact Angle - static [SD]  Contact Angle - dynamic [SD]	Contact angle measurement on a sessile drop without change of volume. **static**: time-independent measurement **dynamic**: measurement as a function of time

MT Type	Templates	Meaning
 Contact Angle - static [SD]  Contact Angle - dynamic [SD]	 Contact Angle - dynamic [SD]  Contact Angle - hysteresis [SD]	Contact angle measurement on a sessile drop with change of volume **dynamic**: online measurement on advancing *or* receding drop margin **hysteresis**: comparative online measurement with alternating advancing *and* receding drop margin
SFE - Measurement --> SFE of Soild Samples	 Using Static Angle measurement  Using Dynamic Advancing Angle measurements	Determination of the surface free energy (SFE) of a solid from contact angle measurements **Using static...**: static contact angles are measured and used for the calculation **Using dynamic...**: dynamic contact angles are measured and used for the calculation

SFE templates must be used for the surface free energy of a solid – the contact angle templates are only intended for wetting tests!

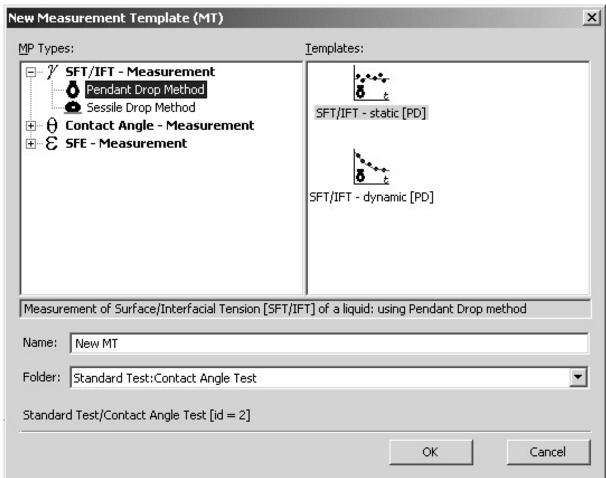
At the top left the basic MT types ("Types") available are shown – these correspond to the program modules ordered.

On the right the prepared templates ("Templates") are listed for the selected type and can be selected per mouse-click.

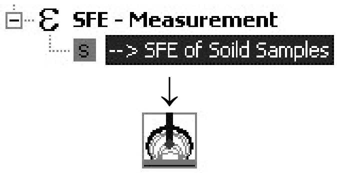
Under "Name" a name is assigned to the MT to be created.

The menu under "Folder" opens the structure tree of the current MT-File for selecting a folder.

The Wizard is started with "OK".

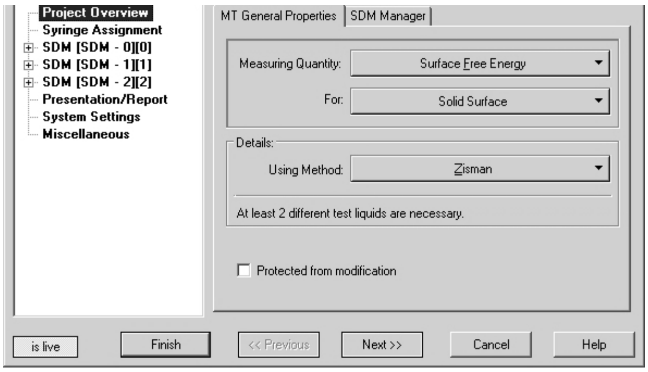


6.1 Guide to the Wizard menu



Using Dynamic Advancing Angle measurements

First select an MT template: the template "SFE"→"Dynamic Advancing..." if available, or otherwise a contact angle MT.
Select a name and a folder and start the Wizard with "OK". After the MT has been placed in the MT data base the first page of the Wizard opens.



You can either selectively choose the individual pages of the menu from the structure tree (left) – or browse through them page by page with the Next button.

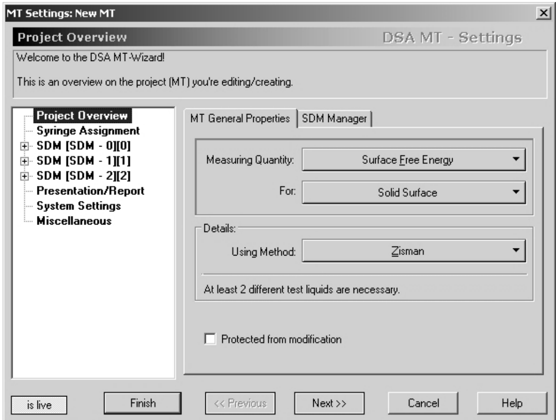
In the Wizard menu open all the menu items under the first SDM ("SDM – 0") (by clicking on the plus sign). The following table helps you with orientation in the manual:

Menu item	Function	page
Project Overview	Measuring method, defining template SDMs	47
Syringe Assignment	Assigns liquids to the syringes	48
SDM [SDM - 0][0]	Enters all parameters for the first SDM	49
System Information	Drop type and measured value to be found	49
Droplet Phase	Liquid used for the drop	50
Substrate Phase	Solid (not for pendant drops)	51
Environment Phase	Surrounding phase (gas or liquid)	51
Dispensing	Dosing mode and flow rate	53
Drop Deposition	Contact with surface (not for pendant drops)	54
Sequence	Dosing, syringe and axis movement sequences	56
Needle Positions	Needle positions defined in the sequence	58
Table Positions	Table positions defined in the sequence	58
Measurement	Mode and timing for drop measurement	59
Computation	Shape analysis parameters	64
Magnification	Determines the magnification scale	68
Imaging Device	Optics parameters	70
SDM [SDM - 1][1]	Parameters for second SDM	
SDM [SDM - 2][2]	Parameters for third SDM (infinitely extendable)	
Presentation/Report	Results-Monitor presentation options	71
System Settings	General system settings (rarely need changing)	72
Miscellaneous	Memory and program start options	75

6.2 "Project overview" – basic MT properties

The project overview contains the two tabs "MT General Properties" and "SDM Manager".

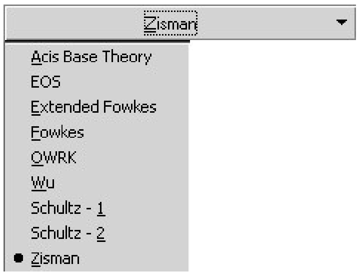
Under "MT General Properties" you will find the measuring quantity for the selected template (in the selected example "Surface Free Energy", SFE). Under "For" the class of substances is shown, in this case a solid ("solid").



The options "Measuring Quantity""(quantity to be measured) and "For" (substance class) should not be altered, as they are automatically defined by the template. You should select a suitable template instead!

The option „Protected from modification" protects all parameters of the MT from unwanted alterations.

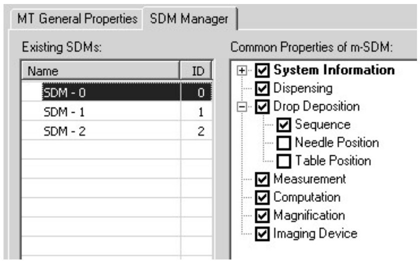
Under "Details" a drop-down menu opens with the evaluation methods for the surface free energy. Select the required method, while observing the prerequirements given below on the tab (number of measuring liquids). Details about the evaluation methods are given in Section 0 on the theory.



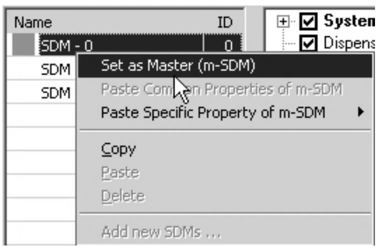
For SFT/ contact angle measurements the field "Details" remains empty.

SDM-Manager: managing and using Master SDMs

The SDM manager contains a list of all SDMs (Single Drop Measurements) belonging to an MT. For SFE-Templates three SDMs are already installed, however, as many as desired can be added.



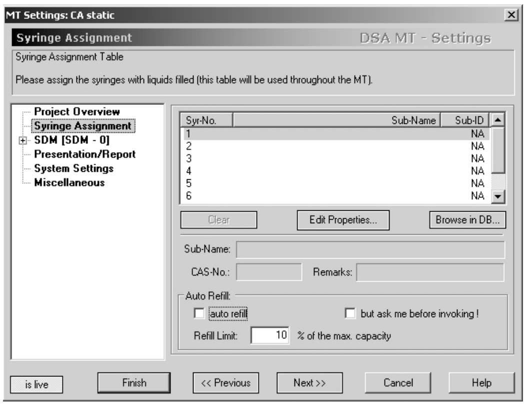
An SDM can be defined as a Master SDM with the menu item "Set as Master" in the context menu. The parameters compiled in the list "Common Properties of SDM" can be copied into other SDMs. Select the destination SDM and select "Paste Common Properties" from the context menu.



Often it is only the dosing position that changes from drop to drop – in such cases it is advisable to take over all the properties of the Master SDM except for "Needle Position" and "Table Position"!

Via the context menu of an SDM you can also copy an SDM ("Copy") and use "Paste" to generate an identical drop measurement to that of the source SDM.

6.3 “Syringe Assignment” – syringe liquids



Motorized dosing systems of the DSA100 can be equipped with up to 8 computer-controlled syringes. Each syringe can have a different liquid assigned to it. The physical and chemical data of the assigned liquid are used as the basis for subsequent calculations.

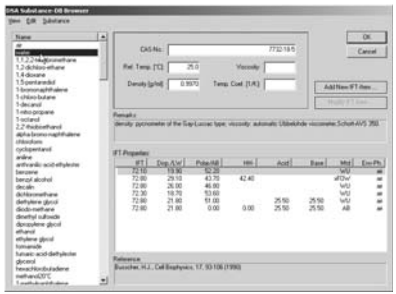
Please make sure that the liquids are correctly assigned to the syringes. The standard occupancy for each syringe position can be found in the DSA100 Manual.

Assignment from the database

First select the syringe to which a liquid is to be assigned.

You only have to assign the syringes to be used for the MT.

The assignment takes place via the liquids database which is opened with the Browse in DB... button. Choose the liquid for the selected syringe and click on “OK”.



For some liquids there are several sources to which the physical data refer. Select the desired entry and click on “OK”.

If available, select the liquid entry according to the desired SFE method:

AB for Acid-Base

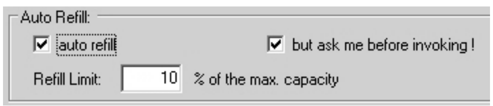
xFOW for Extended Fowkes

or WU

(→ chap. 0)

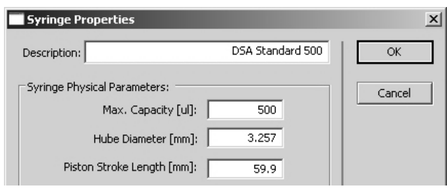
Auto refill

With the auto refill option the syringe is refilled automatically during the run of an MT. The “Refill Limit” sets the filling level (in %) at which the refilling is carried out. With the option „But ask me…“ a dialog appears which must be confirmed before the refilling starts.



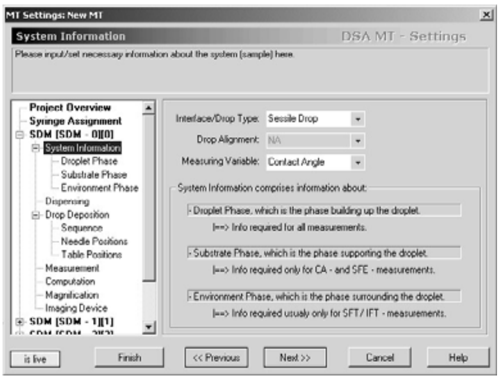
Syringe properties

Under “Edit Properties” you can adapt all the properties of the syringe. This is only necessary if you want to use syringes other than those supplied by KRÜSS.



6.4 System Information – drop type and measuring quantity

This page contains information about the type of drop and the quantity to be obtained by measuring the drop. If, as suggested, you have selected an SFE template then "Sessile Drop" and "Contact Angle" will be set automatically. Do not change the method here, but select a suitable template using the MT Wizard (→ p 44).



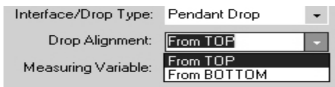
1. **Setting the drop type ("Drop Type")**

"Pendant Drop": hanging drop on which the surface and interfacial tension are to be measured.
Sessile Drop": drop lying on a solid surface whose contact angle, as well as the surface tension, can be measured.
"Captive Bubble": an air bubble trapped in a liquid beneath a solid surface.

The choice between "Pendant" and "Sessile" should not be made here; it is automatically defined by the selection of the MT template at the start.

Only the "Captive Bubble" method needs to be selected here.

2. **Setting the direction ("Alignment")**
(only for pendant drop)



Standard: "From TOP" The drop is hanging at the tip of the needle.
For interfacial tension between a light drop phase and a heavy surrounding phase: "From Bottom". The needle is at the bottom. The buoyancy is keeping the drop upright.

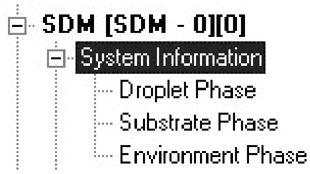
3. **Setting the measured value – ("Variable")**

"IFT" – surface or interfacial tension
"Contact Angle"

The phases in the system are explained at the bottom: drop liquid ("Droplet"), solid ("Substrate") and drop surroundings ("Environment")

A "Substrate" (solid) only exists for contact angles.

6.5 Phase assignment: droplet, substrate, environment

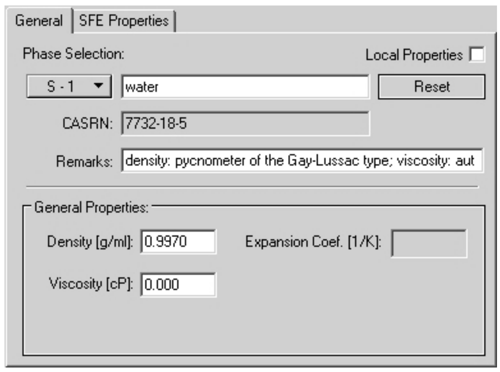


The drops to be measured ("Droplet Phase") have either one or two surrounding phases:

1. Interfacial and surface tension: a gaseous or liquid surrounding phase ("Environment")
2. Contact angle (and corresponding surface free energy measurements): a solid contact phase ("Substrate") and a gaseous or liquid surrounding phase ("Environment").
3. Surface energy determination according to Schultz : Contact angle measurement of a drop phase in a surrounding liquid phase. „Schultz 1" (→ Section 6.5.5) is carried out using a constant drop phase and changing surrounding phases.

The phases are assigned in sequence in the menus "Droplet Phase", "Substrate Phase" and "Environment Phase" – just as for the syringe assignment (see Section 6.3) using the substance database.

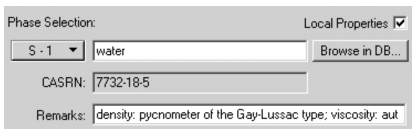
6.5.1 Selecting the drop phase ("Droplet Phase")



The SDM must first be assigned to the syringe (S1-S8 –for manual dosing there is only one syringe: "SM"). If the selected syringe has already been assigned a liquid under "Syringe Assignment" (see Section 6.3) then its name will appear in the upper input field. In order to select the physical data of the liquid the database must be opened again.

With "Reset" the data from the liquid assigned to the selected syringe can be actualized.

The option "Local Properties" is required whenever the liquid in a syringe needs to be replaced during the current MT sequence, e.g. during an SFE measurement with a single dosing system.



With the option "Local Properties" you can suppress the link to the liquid selected under "Syringe Assignment" and use "Browse" to assign a liquid for the current SDM only.

When you deselect this option again and then click on "Reset" the original liquid will be assigned again.

„Local Properties“

Usually the entries for the liquids depend on the syringe assignment. The entries under „Droplet phase" cannot be altered with the exception of „Remarks" .

With the option *Local Properties* a liquid can be assigned to the current SDM independently from the syringe assignment. This option is required if:

- a manual syringe or a Single Direct Dosing system is used.
- the number of required liquids is larger than the number of available syringes.
- a liquid is not entered in the database.
- the liquid parameters to be entered are different from those given in the database.

6.5.2 Solid ("Substrate Phase")

The solid is normally the sample under investigation, so that it can be named manually here. For interfacial and surface tension measurements there is no solid phase.

6.5.3 „Environment Phase“

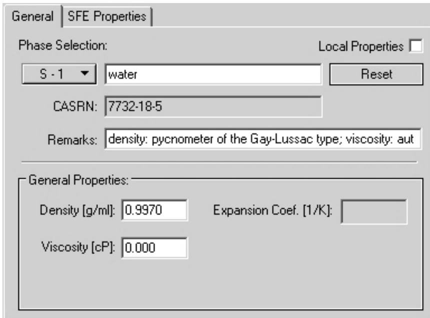
The „environment phase" is a gas in most cases, rarely a liquid (for the captive bubble method, for surface energy determination according to Schultz or for interfacial tension measurements with the pendant drop method). The standard entry is "Air".

6.5.4 Physical Data

These entries are used for later calculations (e.g. SFE)

After transfer from the database physical data will be found on the tabs "General" and "SFE Properties". With the exception of "Remarks" about the liquid used, the values can't be altered here but result from the database entry for the liquid assigned to the syringe.

"General" tab



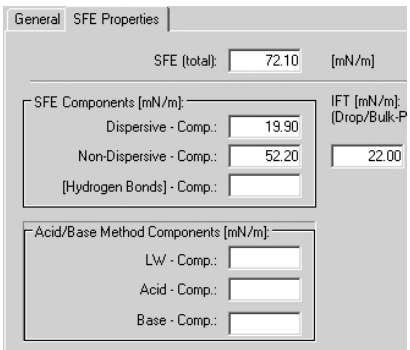
CASRN: „Chemical Abstracts Registry Number" –substance entry in the CAS database.

Density: density of the liquid (for pendant drop and Laplace-Young contact angle measurement)

Expansion Coef: coefficient of expansion of the liquid (only for temperature measurements).

Viscosity: viscosity of the liquid.

"SFE Properties" tab



SFE (total): surface tension (for all contact angle methods)

Dispersive-Comp: dispersive fraction. For all contact angle methods except EOS and acid-base.

Non-Dispersive-Comp: non-dispersive (polar) fraction. For all contact angle methods except EOS and acid-base

Hydrogen B.: hydrogen bridge formation fraction. Only for Extended Fowkes

Acid/Base Method Comp.: All three entries only for acid-base contact angle method.

IFT (Drop/Bulk-Ph.): Only for the "Environment" phase for Schultz 1 and 2: Interfacial tension between the drop phase and the environment phase. .

6.5.5 Phase assignment for Schultz 1

The assignment of the phases changes when using the Schultz 1 method:

- Only one drop liquid is to be assigned. As soon as a liquid is assigned to the first SDM, the text boxes under "Droplet Phase" become inactive for the other SDMs.
- Instead of changing the drop phase, the surrounding phase is altered.
- For each surrounding phase the following information must at least be entered: 1) SFE total; 2) Dispersive Comp.; 3) Non-Dispersive Comp.; 4) IFT Drop/Bulk Phase (interfacial tension between the drop phase and the surrounding phase).

6.6 "Dispensing" – dosing mode and dosing rate

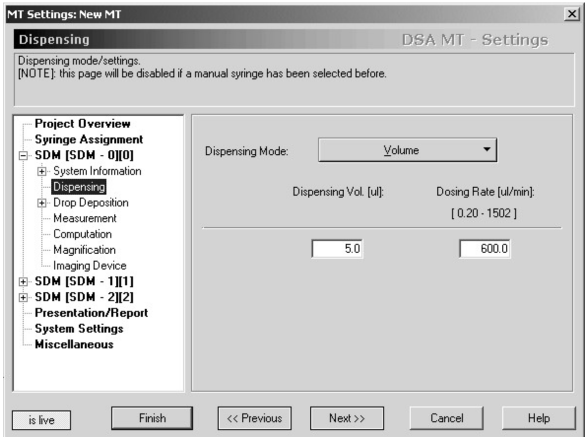
Under "Dispensing" the dosing mode and dosing rate are defined for the SDM according to the syringe that is to be used. If you are only equipped with a manual syringe then the mode "Manual" will be entered here automatically.

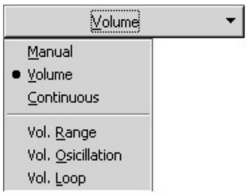
You have already encountered the dosing modes under CPanel. In a similar way you can select the required dosing mode from the drop-down menu.

For pendant drop measurements and static contact angle: "Manual" and "Volume"

For dynamic contact angle: "Continuous" and "Vol. Range"

For hysteresis measurements: "Vol. Oscillation" and "Vol Loop".

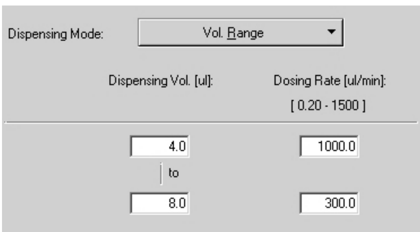




Different modes and flow rates can be defined for all syringes (and SDMs) – however, it is usually advisable to use a common dosing mode (e.g. "Vol. Range" for all SDMs in a surface free energy measurement (SFE) with dynamic contact angles).

How to find optimal volumes: experiment with the CPanel and transfer the parameters you find to the active SDM with the T button!

Volumes and dosing rates are defined exactly as in CPanel (→p. 36). When a dynamic dosing mode is selected different dosing rates can be assigned to the steps.

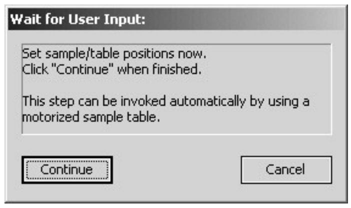


6.7 "Drop Deposition"

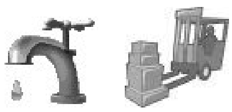
Manual

*With **manual** components you will be guided through the measurement by the dialog window.*

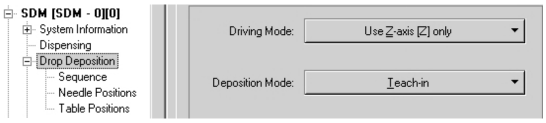
If your DSA100 only has manual syringes and axes then only manual drop deposition is possible. In this case the sample table height must be controlled during the measuring sequence and the drop deposited. Dialog windows guide you through the sequence.



Automatic



For automatic components this is where you make initial decisions about the mode of depositing the drop on the sample. The measuring procedure itself is defined in the following sequence item "Sequence".



Driving Mode

When Syringe Loader?

"Auto Delivery"

Deposit drop

Pendant drop

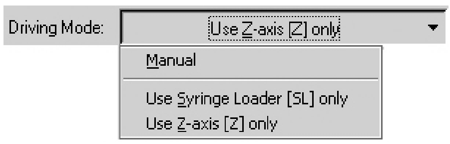
Manual Z-axis

When Z-Axis?

Pick-up drop

Manual dosing system

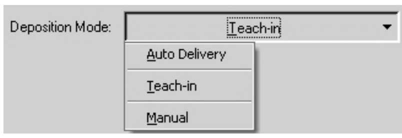
This is where you decide whether during the automatic sequence the movements of the dosing system ("Syringe Loader") or those of the Z-axis are to be controlled.



Please be aware that if „Use Z-axis" is selected only the sample table moves to the "Deposition Position" while the Syringe loader remains in the "Standby"-Position.

Deposition Mode

This is where you determine the degree of automation for positioning the drop. With "Teach-In" defined height positions ("Stand-by" and "Deposition") are used. "Manual" is the setting for a DSA100 with only manual components or to operate your automated DSA100 manually.

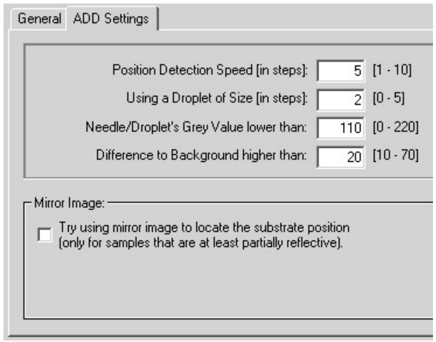


With "Auto delivery" (only for contact angle measurements) the syringe finds the dosing height automatically and deposits the drop there. The "Deposition position" is ignored.

"ADD-Settings": settings for "Auto-Drop-Delivery"

The Auto Drop Delivery function is only used for contact angle measurements on a drop. If the function Auto Drop Delivery has been selected then in the control procedure the needle movements in the video image will be analyzed and the drops automatically deposited on the sample.

On the "ADD-Settings" tab you can make the basic settings for this option.



The "Driving Mode" must be set to "Use Syringe Loader".

"Position detection speed": needle speed during the search. The value 5 (relative value) can normally be retained.

"Using a droplet of size": the surface finding routine in the DSA3 software works more reliably when a small liquid droplet is hanging from the needle (values between 1 and 3 (relative drop size) are normally suitable).

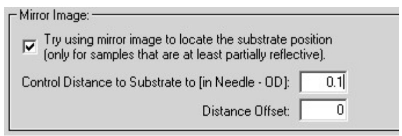
Make sure that you have good optical settings. With automated optics click on "Realize Settings" ⇒ before the start of the MT – this is also what we advise you to do for each MT start.

The value has no influence on the later dosing volume. The value 0 should only be selected when the surface provides a clear mirror image. However, in this case the option "Try using mirror image..." must be switched on.

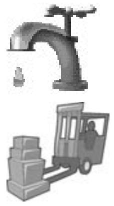
"Needle/Droplet's Gray Value lower than": this value gives a grey value difference for recognizing the needle / droplet in the image. Values around 90 should be used for high-contrast images, higher values (115-130) for low-contrast images.

"Difference to Background higher than": this is where you define the extent to which the gray value transition zones at the margin of an object are to be regarded as belonging to the object. The higher the contrast, the higher the value that should be entered. It is rarely necessary to alter the preset value of 20.

"Try using mirror image": The use of the mirror image when searching for the sample position leads to greater accuracy in recognizing the surface. This option should only be switched on when the sample provides a clear mirror image.



The value for **"Control Distance"** gives the distance to the found sample height – the reference size is the needle diameter in the image (0.1 = 10% of the diameter).
If a droplet is hanging from the needle during deposition then an **Offset** can be set if the needle tip is to move under the point of contact.



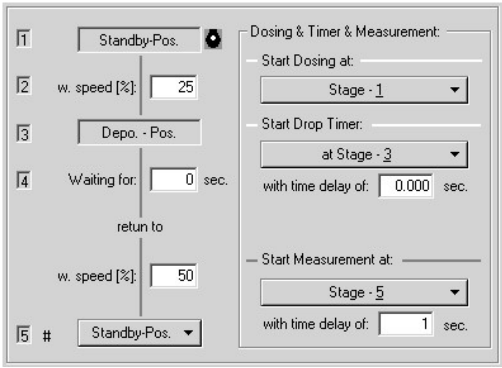
6.8 “Sequence” – movement and measuring sequence

At this point in the Wizard the defined positions “Stand-by”, “Deposition” and “Parking Position” are included in the freely programmable sequence. The run sequence is divided into 5 *stations* (left-hand side); these can have the 3 *tasks* on the right-hand side assigned to them (Dosing, Start drop timer, Start measurement).

The stations

The sequence refers to controlled components (i.e. to the selections “Use Syringe Loader” or “Use Z-Axis”; p. 54)

The numbers 1-5 at the left-hand margin indicate the stations in the dosing/ measuring sequence:



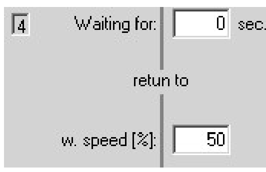
1 First the axes *and* the needle move to the “Stand-by” position.

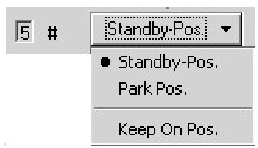
Assignment of the standard positions on the next two pages of the Wizard (“Needle Positions”, “Table Positions”).

2 The needle *or* the axes are on the way to the “Deposition” position (depending on the selection made under “Drop Deposition”; p 54.).
The speed to be set (in %) refers to the speed assigned to the axis in CPanel (→ p. 30).

3 The used component has reached the “Deposition position”.

4 The component (axis or needle) will remain at the “Deposition” position for the period entered under “Waiting for” and will then move – at the set speed – to the position given under 5. With “Keep on Pos.” the Deposition position will not be left.



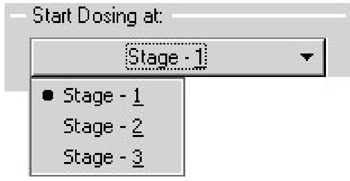


5 The waiting time has elapsed and the used component has reached the assigned position.

The tasks

During the movement sequence three tasks have to be carried out by the DSA3.

1. **"Start Dosing"**: Single generation of a drop or also continuous flow (for dynamic measurements). The start of dosing can take place at Station 1, 2 or 3; i.e. at the Stand-by position, on the way to the "Deposition" position or when the "Deposition" position has been reached.



Stage 1 e.g. for:

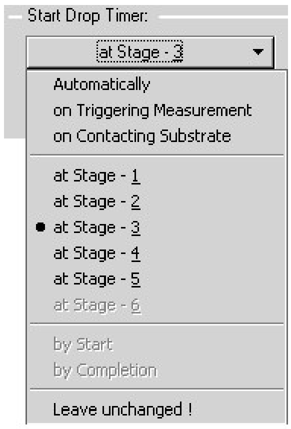
Pendant drop

Deposit/pick up drop

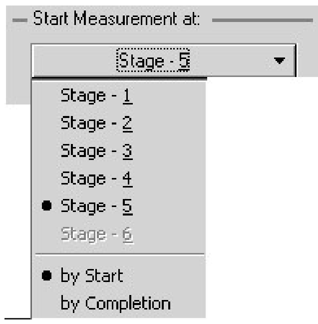
Stage 3 e.g. for:

Dynamic contact angles

2. **"Start Drop Timer"**: starts timing. The drop age is a relevant quantity for measurements. The point during the sequence at which timing is to be started depends on the application.
   You can start measuring the time automatically ("automatically") or link it to an event: the start of the measurement ("Triggering Measurement") or contact with the solid surface (only for "Auto Delivery").
   Of course, each Station 1-5 can also be linked to the start of drop timing. A waiting period ("Delay") can be set for each time.
   If the timer is not to be started then "Leave unchanged!" must be selected.



3. **"Start Measurement"** – the starting point of the measurement in the movement sequence also depends on the particular application. The measurement can be started at each of the stations. You can also decide whether the measurement is to start at the beginning or end of a station – for example right at the ("Start") of a dosing at "Stage 3" (typical for dynamic contact angles) or at the end ("Completion") of a waiting period at Stage 4 (typical for static contact angles).
   A waiting period ("Delay") can also be included at the start of a measurement – for example when a dynamic contact angle measurement is not be started right at the start of dosing.



What is to be measured and how – or whether a video is first to be recorded – depends on the settings made under "Measurement" and "Computation" (on the following pages).

6.9 “Needle” and “Table” positions

In the description of the CPanel you have already encountered the standard positions. When programming an MT you also have the possibility to determine the stored positions “Parking”, “Stand-by” and “Deposition” directly in the Wizard procedure.

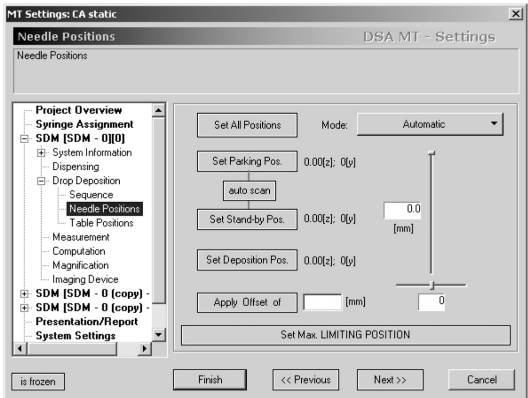
Shortcut keys

Switch: Ctrl>+
s: syringe
x,y,v(!): x,y,z-axis

Control is carried out via the keyboard. You must be able to see the live image – if necessary switch from [is frozen] to [is live] at the bottom left. Use the shortcut keys to select the particular element to be controlled.

Control: <Ctrl>+
<PgUp↑>; <PgDn↓>;
also: ← and → for horizontal needle

The control (“Mode) must be set to “Automatic” – unless you only have a manual dosing unit.



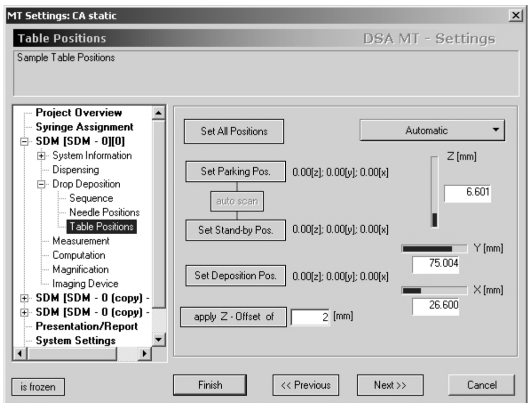
Use the key combinations to move to the necessary positions in succession and in each case click on position fields to save the position. You can also set the current position for all stored positions at once (Set all Positions).

For “Auto-Delivery” the “Deposition” position of the needle is irrelevant!

To adapt the positions to changing sample heights without changing the stored standard positions a displacement of the positions (“Offset”) can be defined.

*For controlling the **Z-axis** always press the <PgUp↑> or <PgDn↓> key **briefly**. Otherwise an automatic switch will be made to the y-axis!*

For syringe control you can use the automatic search (Auto-Scan) for the Parking and Stand-by positions – but the zoom and focus must not be completely out of adjustment during this process!

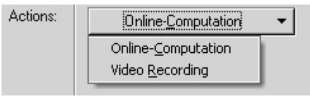


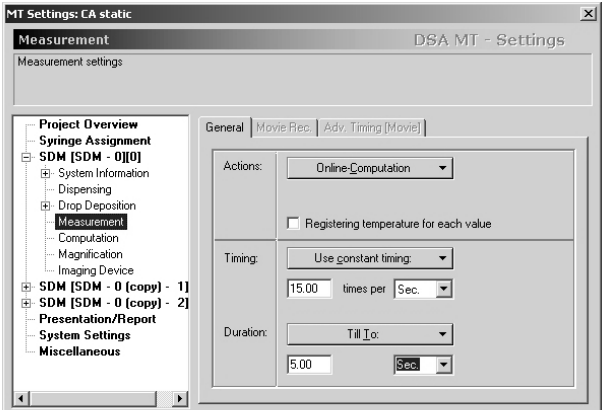
Please note that if the option „Use Z-Axis“ was selected (→ p. 54) only the z-Axis moves to the “Deposition Position” while the syringes loader remains in the “Standby Position” waiting for the table to pick up the drop.

6.10 "Measurement" – measurement or video recording

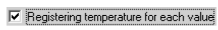
In this step the way of making a measurement – the action "Measurement" - will be covered in more detail in programming the sequence.

The main selection is made under "Actions":





The temperature is either transferred once at the beginning of a measurement or „for each value"if this option is selected.



You can:

- Make the measurement directly on the framegrabber image ("Online-Computation"). Measuring data is recorded as soon as the station defined under "Sequence" has been reached.
- Instead of making the measurement you can first record a video of the run for later evaluation ("Video-Recording"). Instead of the measurement the start of the video recording can also be linked to the defined "Sequence".

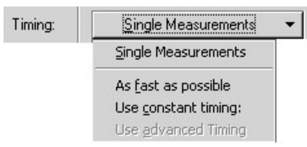
With manual equipment the measurement starts after the drop has been manually positioned and dosed and then confirmed with "Continue".

6.10.1 "Online-Computation" - direct measurement

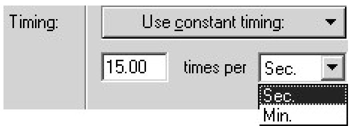
With "Online-Computation" drop image analysis takes place immediately after dosing according to the method set in the next Wizard step "Computation". The number of measured values and the timing of the measurement are defined first.

The settings made here can also be used outside an MT sequence by using the  *button.*

You can trigger a single measurement ("Single Measurement"), or start a series of measurements at as short intervals as possible ("As fast as possible") or at defined intervals ("Use constant timing").



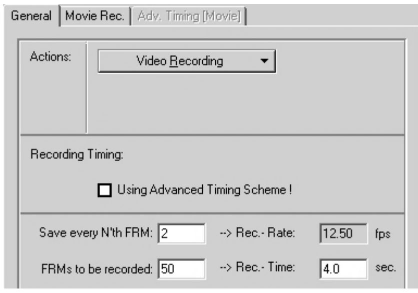
With "Constant timing" you should enter the number of measurements to be made per second or per minute.



The measurement terminates after the time set under "Till To" or when stopped by the user ("Till User Break").

6.10.2 „Video Recording“

Instead of making an immediate recording, with the option "Video Recording" you can record a live video of the framegrabber live image. The length and start conditions are defined in this Wizard step.
The evaluation of the video takes place in a second step within the context of a "Computation".



Length and Timing („General“)

Under "General", settings are made for the length and recording rate (frames/s). The maximum speed depends on the camera that has been installed.

The total number of frames and the total time mutually affect each other.

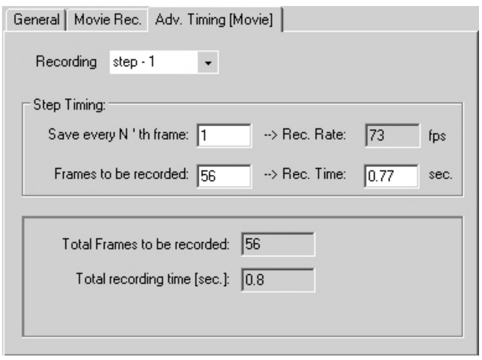
"Save every n'th frame" defines whether every second, third, fourth, etc. frame of the framegrabber image is to be recorded. The image recording rate ("Recording rate") is automatically calculated from this. "Frames to be recorded" determines the total number of frames to be recorded and "Recording Time" the length of the video.

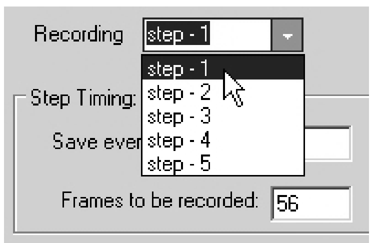
If "Video Recording" is activated for an active SDM then you can start the video outside an MT run with the button.

With the option „Using Advanced Timing Scheme“ the timing options in this tab will be inactive. The timing is programmed in the tab „ „Adv. Timing [Movie]“ instead which is active then.

Extended timing options

On the "Adv. Timing [Movie]" tab you can program a time sequence in a maximum of five steps. Each step can have its own image recording time and rate assigned to it. In the lower part the total number of frames and the total recording time are shown.

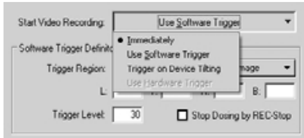




Options for video recording (“Movie Rec.”)

The start of a video recording, like that of a measurement, is linked with the settings under “Sequence” – each of Stations 1-5 in the dosing sequence can be linked at the start of video recording. There are three options:

1. You can start recording immediately after reaching the station selected under “Sequence” (→S. 56).
2. After the station has been reached you can let DSA3 wait until something changes up to a certain height level in the image or region of the image before starting to record (“Use Software Trigger”→ next page).
3. When working with a tilting table you can let recording start when the tilting motion of the table starts (“Trigger on Device Tilting”).



In all 3 options you can use ☑ Stop Dosing by REC-Stop to stop dosing automatically when the recording is finished.

Working with the "Software Trigger" function

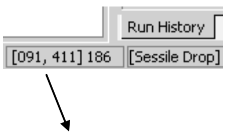
If the option "Use Software Trigger" has been selected then DSA3 will wait until the grey level value alters in a certain region of the image before starting the video recording. The "Trigger Level" defines how large the alteration must be for the image event to trigger the start – the value 30 does not normally need to be altered.

When selecting the image region to be observed you have 2 possibilities (see illustration on right):

Lines that have "vanished" can be found at the upper or lower screen margin.

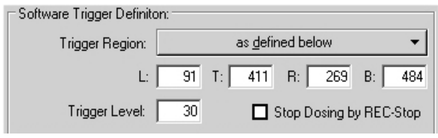
1. The start of recording can depend on a height line to be set in the frame-grabber image ("as Set by Trigger Line on Image"). The trigger line is the lower of the two blue lines in the frame-grabber image. This line is moved by drag-and-drop.

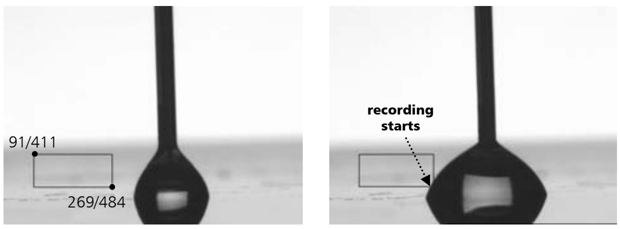
For orientation the position of the mouse cursor in the "Image View" window is shown in the status line:



[horiz. / vert.]

2. The start can depend on changes in a particular image region ("as defined below"). This region is a rectangle (which cannot be seen in the frame-grabber image) whose corner points are defined by pixel coordinates.





Video compression

In the upper part of the screen the video can be stored in a compressed format in order to save memory space ("Use Compression"). Auto-Compression should be selected if the available hard disk memory space is not known.

6.10.3 Saving, playing back and evaluating videos

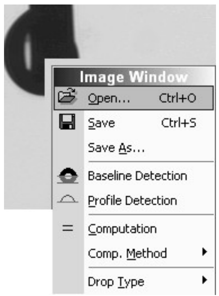
The evaluation of the video cannot be carried out directly while an MT sequence is being carried out. The video must first be saved and then evaluated later.

Save

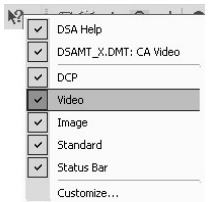
At the end of the video recording a standard dialog opens for saving the file.

Playback

To play back a video it must first be opened, e.g. by using the context menu of the framegrabber image.



The playback icons are activated via the context menu of the symbol bar:



The video can be played back with the 4 buttons :

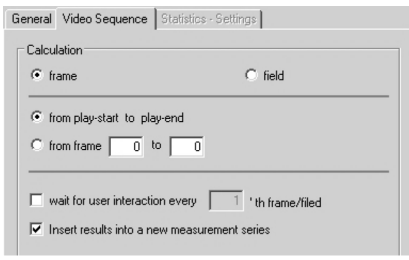
=Stop =To first frame

=Start =To last frame

With the button you can, as an alternative to , record a video outside a running MT. However, the active SDM must be set to video recording, and not to "Online-Computation".

Evaluate

Under "Computation" in the SDM's settings you will find the "Video Sequence" tab for setting the evaluation options.
The calculation can be based on "Fields" or "Frames. In addition you can either select the whole video "from ...to end" or select a section between the two frames defined below.

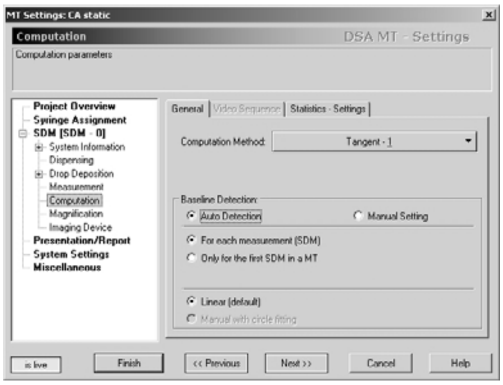


A "Field" is a half-image with half the pixel density, but with double the image rate/s.

The evaluation of the video is started with the button C and is carried out according to the method defined under "Computation".

Start the video evaluation with the icon C .

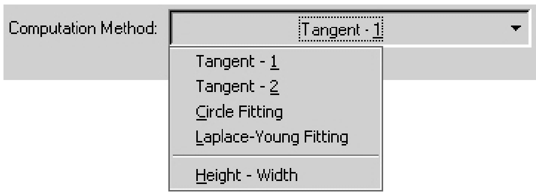
6.11 “Computation” - drop shape analysis



The model used for the drop shape analysis is selected under “Computation”. For contact angle measurements the options for determining the baseline are also defined.
In addition the way in which the mean value is obtained can also be defined (“Statistics Settings“ tab).

6.11.1 Evaluation methods

The evaluation method is defined under “Computation Method”.



Use

for static measurements, 2 contact angle values (left and right)

Tangent-1: The whole profile of a sessile drop is fitted to a general conic section equation. The derivative of this equation at the baseline gives the slope at the three-phase point of contact and therefore the contact angle.
With very flat drops, frequently the fit does not work. Therefore, when an evaluation with “Tanget-1” is not possible, the method “Circle Fitting” is selected automatically.

for dynamic measurements, 2 contact angle values (left and right)

Tangent-2: The profile of the sessile drop in the region of the baseline is fitted to a polynomial function. From the obtained parameters the slope at the three-phase point of contact at the baseline and from that the contact angle is calculated.

for static measurements with small contact angles; 1 contact angle value

Circle Fitting: This method is used for small contact angles (<20°) preferably. The drop shape is fitted to a circle segment equation. With this method, the whole drop shape is fitted and not only the base line region. Therefore, the needle must not remain in the drop

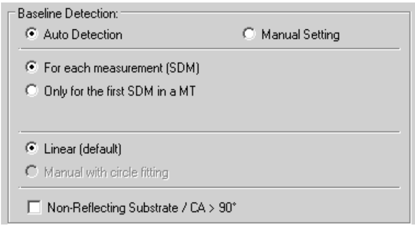
for static contact angle and pendant drop measurements. Most accurate method, but with time consuming calculations.

Laplace-Young-Fitting: The drop shape is described mathematically using the Laplace-Young equation for curved interfaces. This method serves to calculate the surface tension of a pendant drop, but sessile drops (without the needle tip inside the drop) can be analysed as well.

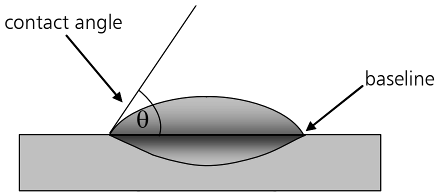
as Circle Fitting, but less robust

Height-Width: As for the Circle Fitting the drop shape is considered an arc of a circle of which the height and the width is measured. However, the “Circle Fitting” should be preferred since the “Height-Width” method uses a smaller amount of contour points.

6.11.2 Determining the baseline (“Baseline Detection”)



The baseline of a drop image is the boundary between the solid surface and the drop. It can be determined automatically from the drop image (“Auto Detection”) or be set manually.



Make sure that you have a bright, sharp and high-contrast image!

For all baseline methods you can decide whether the baseline is to be newly determined for each SDM (“For each Measurement…”) or whether a baseline is only to be determined for the first SDM and then used for all other SDMs (“Only for the first SDM…”). This second method saves an intermediate step, but should only be used when the sample surface is absolutely even.

Automatically detected baseline (”Auto Detection“)

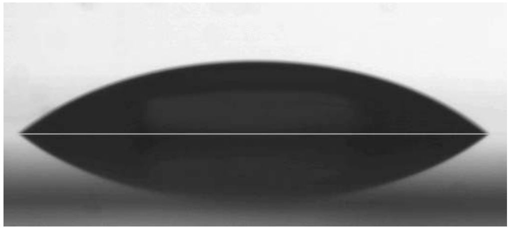
In order to ensure proper baseline detection details about the drop image must be provided:

- For reflecting samples and contact angles below 90°, the option „Non-Reflecting Substrate / CA>90°“ must not be selected.
- For non-reflecting samples and/or contact angles of or above 90°, the option „Non-Reflecting Substrate / CA>90°“ must be selected.

Linear manual baseline („Manual Setting“ + „Linear“)

In measurements with a manual baseline the DSA3 waits until the baseline has been set and its correct position has been confirmed.

For some non-reflecting samples and images with poor contrast, the baseline cannot be detected automatically. In theses cases, the baseline must be set manually using the option “Manual Setting”.



The baseline can be seen in the drop image as a blue line. Click on it in the drop image.

You can alter the **height** of the line by clicking on it and dragging it – or by using the cursor keys ↑ and ↓.

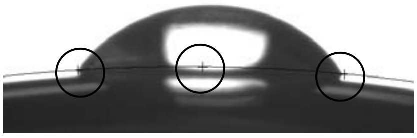
To adjust the **slope** use the cursor keys ← (left side down) and → (right side down).

Curved baseline („Manual Setting“ + „circle fitting“)

With the option ”Manual with circle fitting” a curved baseline can be defined:

With a curved baseline the only contact angle methods possible are ”Tangent 1” and ”Circle”

Three moveable curvature points define the degree of curvature of the curve.

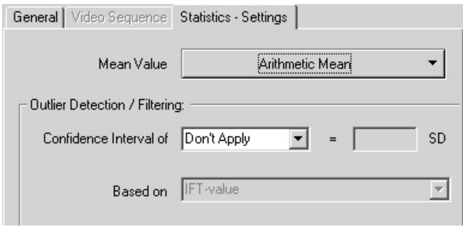


The height of the curve in the image is determined by clicking on it outside the curvature points and then moving it.

☝ Place the two outer points on the phase contact points of the drop and then set the curvature by setting the middle point on the curvature of the surface.

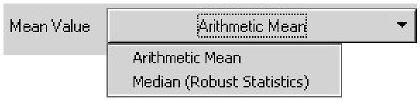
6.11.3 Mean value calculation (“Statistics Settings”)

A mean value is generated automatically for the data obtained with an SDM. Settings for the calculation are made under “Statistics-Settings“.



The mean value appears in the Results-Monitor in the first line “SUM” of the data record.

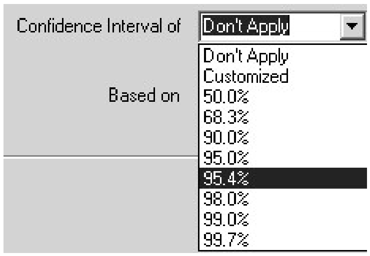
In principle you can choose between the arithmetical mean value and the median. The median is somewhat less sensitive to outliers; however, for uniform running measurements the arithmetical mean value is to be preferred.



You can also later edit the parameters for calculating the mean value:

“Options” in the context menu of the result window.

Further down you can select a reliability level (”Confidence Interval”): only those measuring points that are within the set percentage are used to calculate the mean value. To the right the standard deviation (“SD”) resulting from the given percentage is shown. With “Don’t Apply” all the values will be used for the calculation.



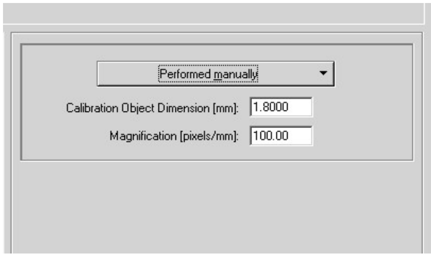
The measured quantity to which the confidence level is to apply is selected under ”Based on”.

6.12 Magnification

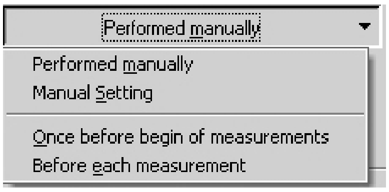
The magnification is needed for SFT/IFT measurements and can only be determined when the MT is drawn up using an IFT/SFT template!

You do not need this Wizard page for contact angle measurements.

Absolute drop dimensions are required for measuring the surface and interfacial tension. Thus, the image scale (in pixels/mm) must be determined.



The mode for the image scale determination is selected in the dropdown menu above the text boxes.



☝ The option "Manual Setting" is not implemented yet; it shows the same behaviour as the option "Performed manually"

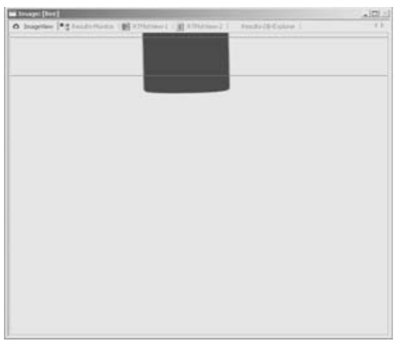
☝ If the image scale is already known (e.g. when working with a loaded video image) its value can be entered manually in the text box "Magnification". However, in this case the two lower options for automatic scale determination must not be selected.

6.12.1 Determining the Magnification manually

DSA3 uses the needle visible in the image as the reference size. For pendant drops a special needle is used of which the diameter must be determined. When this is done, enter the diameter in the "Calibration Object" text box.

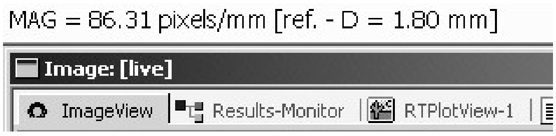
Move the needle into the upper part of the image and set zoom and focus so that the image of the needle occupies about 1/5 of the height and width of the screen.

Define the needle position with "Set all Positions" and also save the current optical settings (→Section 6.13).



After closing the Wizard you require the two blue lines in the image (one can be found at the upper screen margin) for determining the diameter. Move the lines to the height of the needle so that they form a rectangle with the needle contour.

Click on the. ·I . button to determine the magnification. Then click on T to transfer the magnification to the active SDM. The magnification is also shown in the information line above the video image.

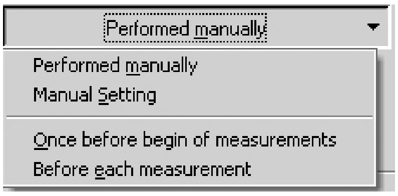


Each time that the zoom is altered the magnification scale must be re-determined!

Transfer the magnification to the current SDM with the transfer button T .

6.12.2 Automatic determination in the course of the measurement

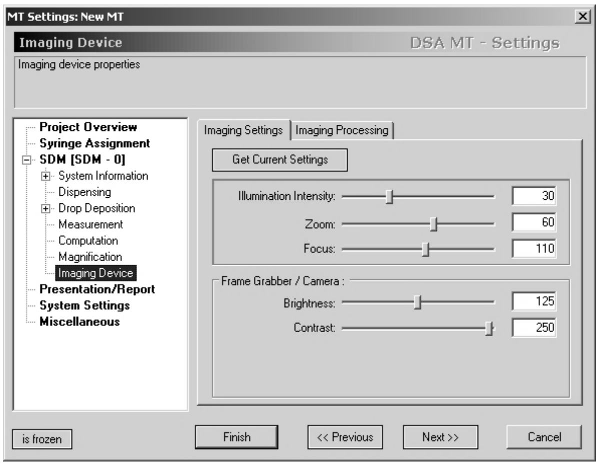
Select one of the two lower options in the dropdown menu:



- *„Once before begin of measurements"*: The scale is measured once after the SDM is started. The resulting scale is used for each individual measurement of the SDM.
- *„Before each measurement"*: The scale is re-determined for each individual measurement of the SDM.

Set the two lines as described above so that they both cross the shape of the needle during the actual run of the SDM.

6.13 “Imaging Device” – settings the optics



In the Wizard step “Imaging Device” the basic settings for the optics are made: the settings for the illumination, zoom and image sharpness (focus) and the control of the threshold value for the drop shape analysis.

Optical settings (“Imaging Settings”)

You are already familiar with the control of the illumination, zoom and image sharpness (when the corresponding components are present) as well as the framegrabber settings from CPanel (→p. 38). You can define the correct settings for the parameters for the SDM directly in the Wizard.

Shortcut keys

Switch: <Ctrl>+

i: illumination

f: focus

z: zoom

Control: <Ctrl>+

PgUp↑: increases value

PgDn↓: decreases value

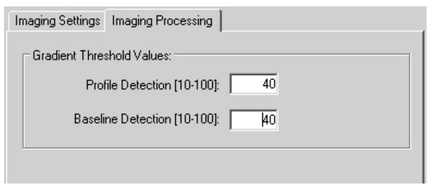
Set the illumination, zoom and focus using the keyboard and click on the button 

to update the value on the tab.

With IEEE-1394 cameras, changing the settings for „Brightness“ and „Contrast“ usually shows no effect.

Threshold values (“Imaging Processing”)

The threshold values set under “Imaging Processing” determine the gray level difference for the recognition of the drop profile (“Profile Detection”) and the baseline “Baseline Detection”.



If you make sure that your image settings are good then you do not have to alter these values.

6.14 “Presentation Settings” –Settings for the Results-Monitor

In the Wizard step “Presentation Settings” you can make the settings for presenting the data in the Results-Monitor. Irrespective of what you select here, all the measured parameters will always be saved in the database.

The settings made here are only used for a preview. The real results management takes place in the “Results-Database”.

Under “Table” and “Chart” you can define the measured quantities for presentation in the table and in the two graphical plots in the raw data display.

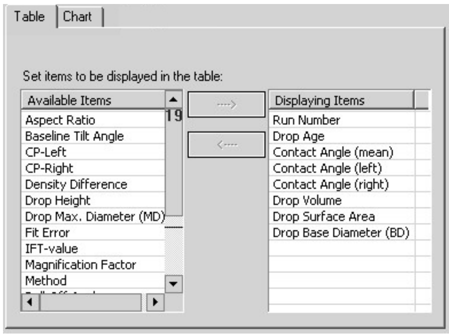
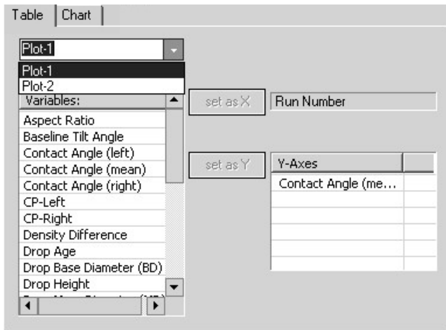
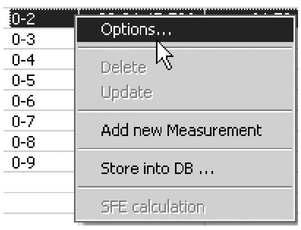


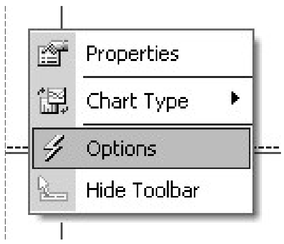
Table: The list under “Available Items” contains all the items that can be shown, “Displaying items” contains those that are already being shown. Select the item by clicking on it and transfer it from one list to the other by using the arrow keys.



Charts: In the drop-down menu select which of the two plots you wish to alter.
The assignment takes place as in “Table”, but you can only select one item for the x- and y-axis.

All these settings can be altered later in the Results-Monitor by selecting the menu item “Options” in the context menu of the data table or of the plot.

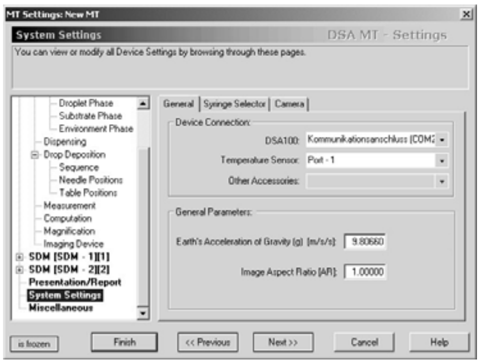




7 “System Settings”: hardware settings

Settings made here are used globally and not only for the current MT.

7.1 Connections (“Device Connection”)

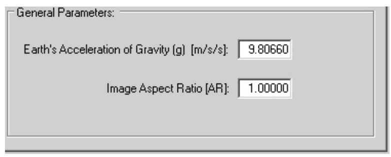


Under “General” the computer port (serial interface) for connecting theDSA100 and, if required, the connection used for the temperature sensor are entered (→DSA100 Manual).

7.2 „General Parameters“

Improper alterations here could mean that all the results obtained are incorrect!

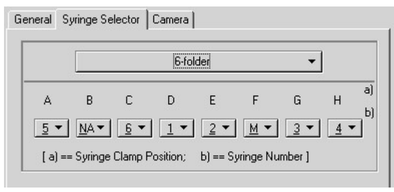
The acceleration due to gravity can be entered below; its value is relevant for the Young-Laplace fit.



The “Aspect Ratio” describes the length/width ratio of the framegrabber image presentation. For components supplied by KRÜSS the value of 1.00000 must never be altered.

7.3 Syringe position assignment – “Syringe Selector”

Here you can alter the assignment of the positions for the syringe numbers. The number of the syringe in the dosing system is selected in the upper menu, the assignment takes place below.



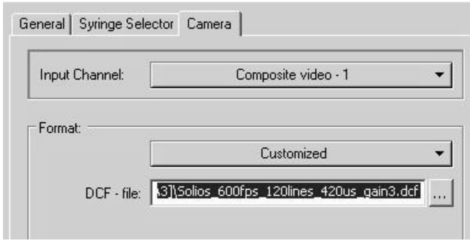
The DSA3 basic settings correspond to the occupancy described in the DSA100 Manual; this means that normally no alterations need to be made.

7.4 „Camera“ – image size and frame rate

If a standard camera with a Falcon framegrabber is installed, no alterations have to me made in this tab.

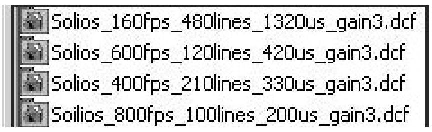
7.4.1 Camera module CF322x (High-Speed-Option)

For a high-speed camera, the actual speed (in fps) depends on the settings in this tab sheet. Under “Format”, the option “Customized” must be selected. With the browse button ... a prepared DCF-file can be loaded which assigns the desired frame rate to the DSA3 settings. These DCF-files are located on the DSA3 CD-ROM in the folder “Cameras/P1H/DCF“. In a second step, settings in the camera software “PFRemote” must be made.



The file name of the DCF-file contains information about the settings for the high-speed camera.

The first part (“x fps”) contains information about the desired frame rate.



It is a good idea to copy the DCF files from the DSA3 CD-ROM to the DSA3 installation folder.

The second part (“x lines”) indicates the height of the frame grabber image.

The third part (“x us”) indicates the exposure time in µs.

The fourth part (“gain x”) shows the gain to be set.

To achieve a higher frame rate the image height is reduced

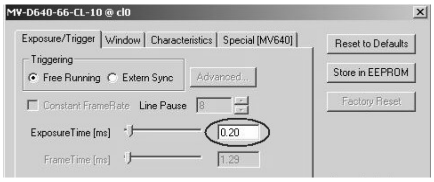
Select the DCF-File for the desired speed.

Camera settings

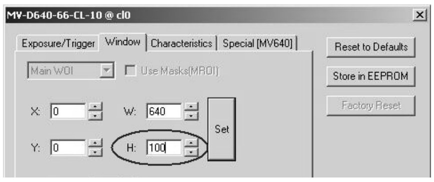
The high-speed settings fort he camera are made in the software “PFRemote“. This program can be started from the Windows start menu after its installation (→DSA100 manual).

Adjust the parameters in PFRemote to the values indicated in the DCF file name as shown on the previous page. Do not change any parameters other then those shown below.

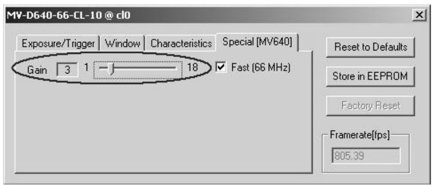
Tab sheet “Exposure/Trigger”:
Set the “Exposure time” to the value indicated in the DCF file name.



Tab sheet “Window”:
Set the window height “H” to the value indicated for “lines” in the DCF file name.



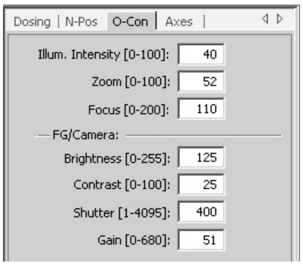
Tab sheet “Special”
Set the “Gain” to the value indicated in the DCF file name.



7.4.2 Camera module CF321x (for the IEEE-1394 interface)

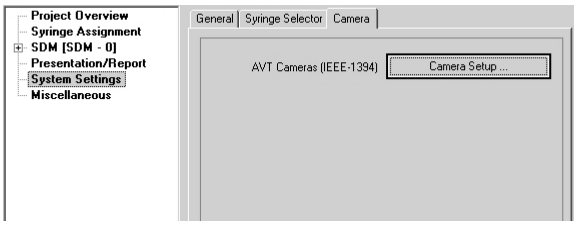
The optional IEEE-1394 camera is connected via the corresponding interface (IEEE 1394 B) and works without a frame-grabber. Settings in two tabs are necessary in order to set the frame rate and get a proper image:

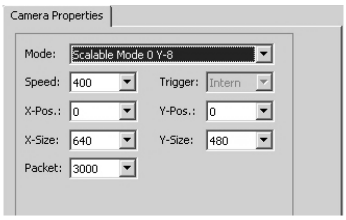
- Shutter and gain on the "O-Con" tab of the Control Panel.



The settings for "Brightness" and "Contrast" have usually no effect when working with an IEEE-1394 camera.

- Image size and image area on the "Camera" tab under "System Settings".



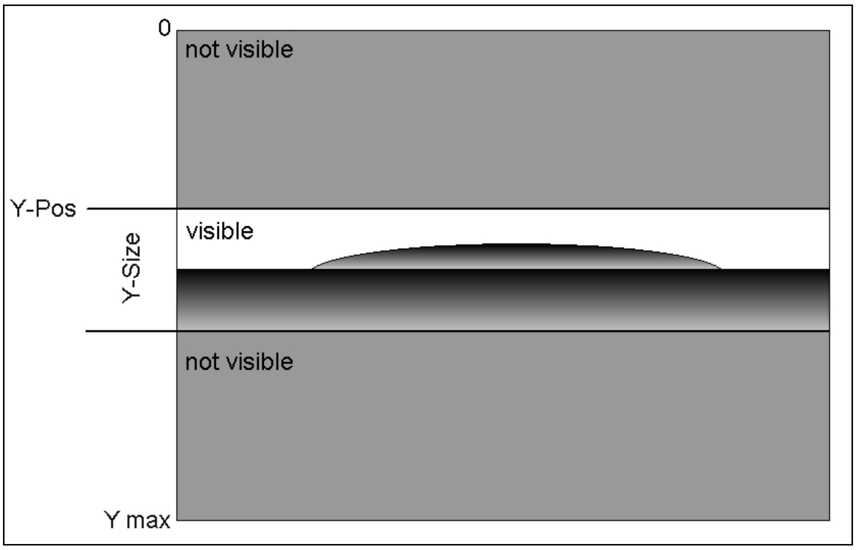


Preliminary settings

- Select the „Scalable Mode 0 Y-8" from the drop-down list box "Mode".
- Select the value 800 from the drop-down list box "Speed".

Setting the resolution (image size and area)

In order to achieve higher frame rates, usually the height of the image (”Y-Size”) is reduced. A reduction of the width (”X-Size”) is also possible. In order to ensure that the object is located within the recorded area the position of the visible area (”X-Pos“ and ”Y-Pos”) can be defined. The following illustration shows the procedure using the image height as an example.



Proposed settings

The settings listed in the following table are only guidelines. Other combinations of values for the „Shutter“ and „Gain“ as well as the resolution are possible.

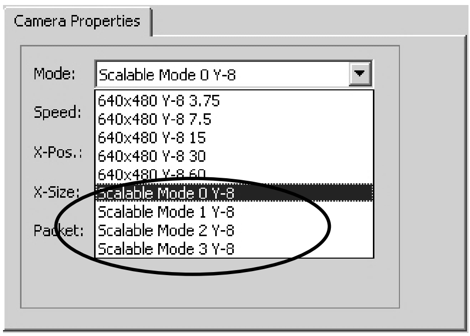
☝ The „Gain“ should be set as low as possible for a certain frame rate.

frame rate	*resolution*	*shutter*	*gain*
25 fps	780x580	2000	0
50 fps	780x580	1000	0
62 fps	780x580	500	0
108 fps	780X300	50	400
183 fps	780x150	50	400
311 fps	780x60	50	400

Explanation of the parameters

For user-defined frame rates, the suitable or necessary parameters must be determined experimentally. The meanings of the parameters on the two tabs shown on p. 75 are given below:

- **Brightness/Contrast**: brightness and contrast settings for the camera image. These values should not be altered; the control of the image brightness should be carried out on the illumination unit.
- **Shutter**: exposure time. The higher the required frame rate, the shorter the shutter value that must be set.
- **Gain**: amplification of the image signal. The value is linked to the shutter speed: the shorter the exposure time, the smaller the amount of light that falls on the camera chip, so that at short exposure times a higher gain value must be set.
- **Mode**: various predefined camera settings for the “Camera Properties” tab can be selected here. For DSA3 we recommend the “Scalable Modes” which the help of which the image size can be varied. With the other ”Modes” the frame rate can be reduced at full resolution which is not sensible in most cases.



Alterations on the tab are assigned to the currently selected “Scalable mode” and saved in this mode; this means that you can define various scalable modes with your own standard settings.

- **Speed**: this value defines the bit transfer rate (max. 800 MBit/s); this setting should not be altered.
- **X-Size; X-Pos**: width and horizontal position of the image. If the image width (“X-Size”) is reduced then the horizontal position of the visible area of the image can be defined via “X-Pos”.

- **Y-Size; Y-Pos**: height and vertical position of the image. If the image height ("Y-Size") is reduced then the vertical position of the visible area of the image can be defined via "Y-Pos".
- **Packet**: size of the data package during transmission. This value is calculated automatically and should not be altered manually.

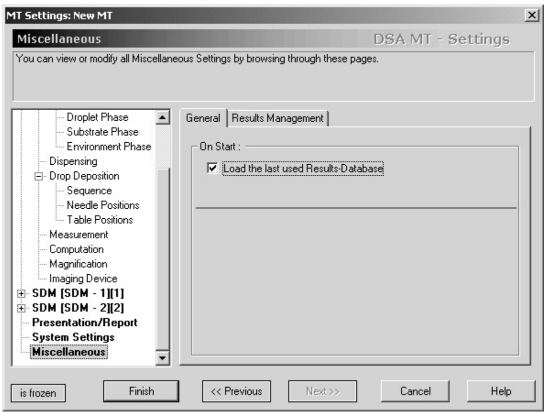
Checking the image rate

The current image rate is shown in the status bar at the bottom right. However, after it has been reset it takes some time for the new value to be shown.

To have the value indicated immediately you can quit and re-start DSA3.

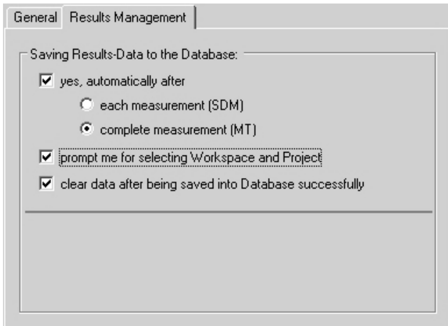
7.5 "Miscellaneous" – initial database settings

In the final Wizard step you can define the basic database settings for the MT.
The tick under "General" ensures that the last Results-Database to have been opened is always called up at the next program start.



Automatic results management

On the "Results Management" tab you can ensure that after each completed SDM or each completed MT the measuring data is saved automatically in the Results-Database.
"Prompt me..." ensures that before data is stored a dialog opens for selecting the main folder "Workspace" and the project.



"Clear Data..." automatically deletes the data saved in the database from the working memory after each measurement – it does not appear in the Results-Monitor, which is only used to display the raw data to make a pre-selection for the database.

8 Results management

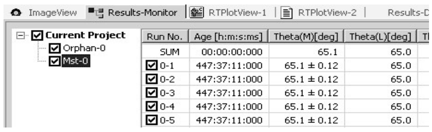
You can also avoid the Results-Monitor and save the data directly in the database after the measurement (→ Section 7.4.2)

The results of a measurement are first collected in the "Results-Monitor". They can be assessed there and in the two associated plots ("RTPlotView"), so that they can be transferred to the Results-Database where the evaluation itself is carried out ("Results-DB").

8.1 Raw data overview ("Results-Monitor")

The generated measuring data is buffered as raw data in the "Results-Monitor". Here it can be assessed and then stored permanently in a database afterwards. In addition the raw data can be shown graphically in two different plots.

The "Results-Monitor" is a data table in which all available data is listed for each individual measuring point of the generated measurement series.

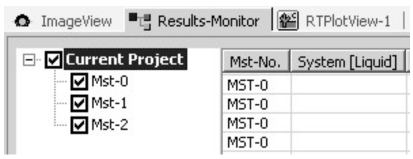


Measured data lists

Measured data can be generated in one of three ways:

1. From an MT run
2. From a series of measurements with the settings of the active SDM
3. From one or more single measurements

In the first two cases a new data series will always be generated in the Results-Monitor. In the third case the values will be appended to the last measurement series that has been generated. Each measuring series contains the name "MST" for "Measurement" and a consecutive number.

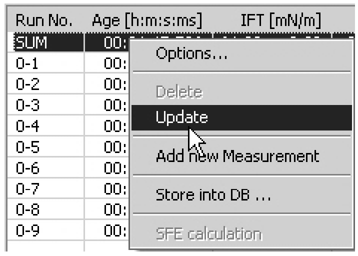


If no measuring series was open then a measuring series generated from single measurement data will be shown as "Orphan".

Recalculating the mean value

The top line of a series of measurements marked with "SUM" contains the mean values for each parameter of a measurement series.

If a measuring series has been generated from an SDM then the mean value will be calculated automatically using the mean value options defined there. If you add data to a measuring series or if you subsequently alter the mean value options (context menu→ "Options"), then the mean value calculation must be updated.



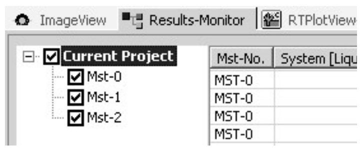
This is done by clicking on the SUM line with the right-hand mouse key and selecting "Update".

Transferring the measuring data to the database

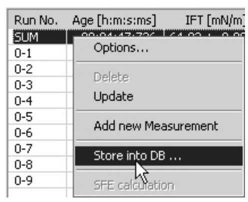
The required measuring series are copied from the Results-Monitor to the database ("Workspace") using the context menu. Further steps such as the calculation of the surface free energy or drawing up measurement reports are only carried out there.

Transfer the required measuring series to the database by using the context menu (right-hand mouse key).

Assess the data and tick those measurements that you wish to transfer to the database.

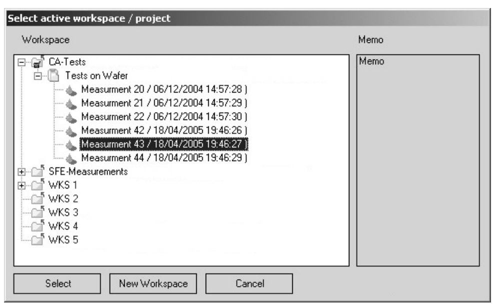


To finally transfer the data to a Results-Database you must select the command "Store into DB" from the context menu. A dialog opens in which you can select and open a main folder ("Workspace") or a project in the current database or also generate a "new Workspace".



If no database is available:

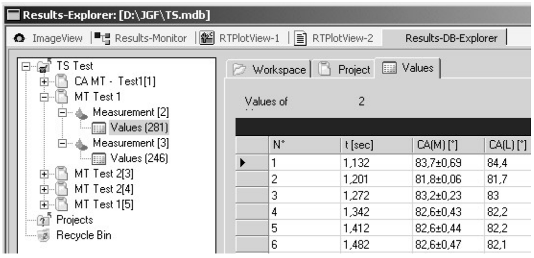
"New Database" in the context menu of the empty Result-DB explorer.



8.2 The results-database ("Results-DB")

The complete management and evaluation of the measuring data takes place in the "Results-DB-Explorer":

- Viewing and structuring
- Calculating the surface free energy
- Drawing up charts and reports



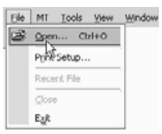
The database is arranged in a tree structure as follows:

- Workspace
  - Project
    - Measurement; single drop → Report
      - Values
      - Diagram („Chart")
    - Report („Value Analysis"; SFE; „Mapping Analsysis")

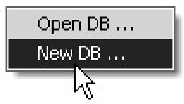
Right at the bottom there is also a "Recycle Bin" in which deleted database items are stored until they are restored or permanently deleted.

8.2.1 Generating a new database

If a database already exists then it can be opened with "Open DB..." - or from the main menu:

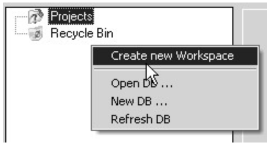


When the program is started for the first time there is no database loaded. To generate a new database open the context menu of the empty area of the Results-DB-Explorer tree and select the option "New DB".

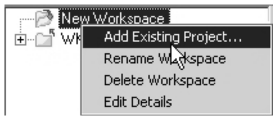


In the dialog select a folder and define the file name of the new database.

8.2.2 Creating and managing workspaces

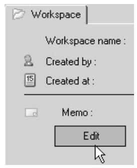


You can use the context menu of the database to create a workspace (“Create new Workspace”.)



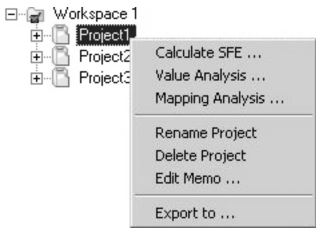
Using the context menu of a workspace, projects can be copied from other workspaces of the same database into the selected workspace with the menu item „Add Existing Project…“.
The Workspace can also be renamed using the context menu (“Rename”), deleted, or you can write an information text for the Workspace (“Edit”).

The infotext can also be entered directly via “Memo”:



8.2.3 Projects

Data measured by an MT is collected in a “project” when saved in the results database.

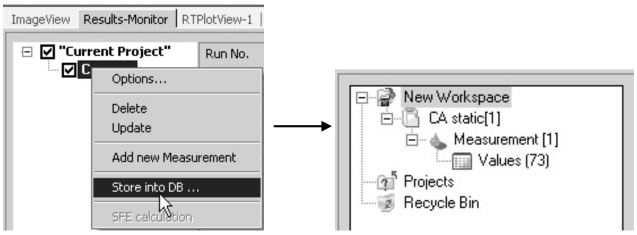


Several measurements on individual drops belong to a project; these can be evaluated from different points of view. The appropriate options can be selected from the context menu of the project:

- From measurements with different drop liquids it is possible to calculate the surface free energy of a solid (“Calculate SFE”) – provided that the data has been recorded with an MT intended for SFE (→Section 9.2).
- Several measurements with the same drop liquid can be evaluated with a “Value Analysis”, in which the mean values of the individual measuring data can be calculated for several or all drops of the project (→p. 90).
- Data of a mapping measurement is also collected in a project and can therefore be subjected to a “Mapping Analysis” (→Section 10.3).

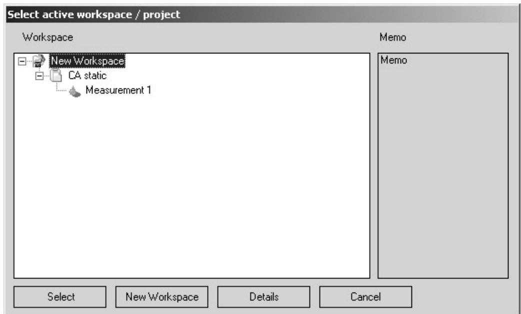
Generating a project

Projects are generated on saving data from the Result Explorer (or directly after a measurement, depending on the settings (→p.75).



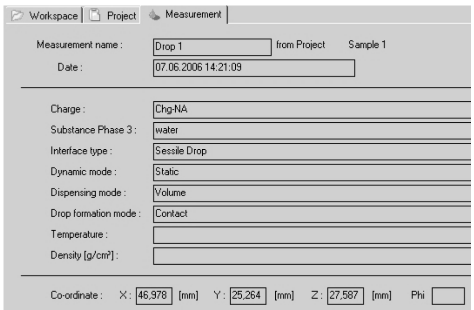
The name of an item is first generated automatically; the name of the project depends on the MT used for the measurement.

For transferring data from the "Results Monitor" either an existing Workspace can be selected ("Select") or a new one can be generated ("New Workspace"). A new project will be generated in the selected Workspace with the name of the MT used.

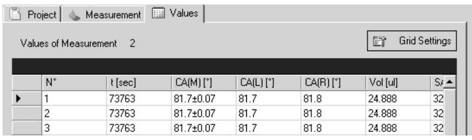


Measurements

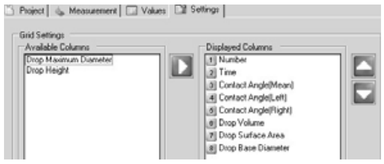
If you click on a measurement a tab will appear giving information about the measurement parameters. As these result from the MT-parameters they cannot be edited.



Values



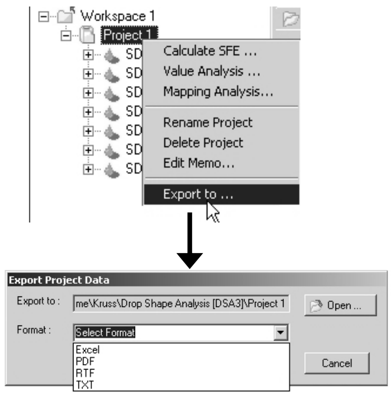
The values obtained during a measurement are listed under “Values”.



With “Grid Settings” you can select the quantities to be shown in the table. The quantities still available are shown in the left-hand column; those to be shown in the right-hand one.
Click on the corresponding column and compile the list of “Displayed Items” by using the arrow keys or . The order of the columns from left to right in the resulting table is defined by the order of the items in the list “Displayed columns”. You can change this order with the arrow buttons and .

Batch-Export of measurements

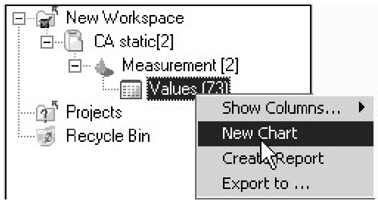
You have the possibility of exporting all the measurements belonging to a project to a different data format with a single command.



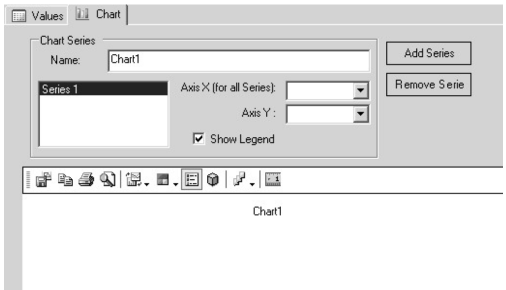
Open the context menu of the project and select the command “Export”.

Then select the format in which the data is to be stored. Under “Open” you can select the folder into which the export files are to be copied.

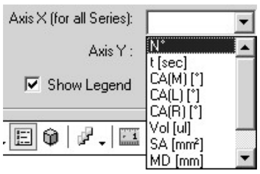
8.2.4 „Charts“



To generate a chart open the context menu of a measurement or a measured value entry in the structure tree of the database.



When generating a chart you must define a quantity for the X-axis; you can then place several quantities (“Add Series”) on the Y-axis.



With “Show legend” you can reveal and conceal the legends.

In the toolbar above the chart you will find numerous layout possibilities.

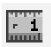
Managing charts

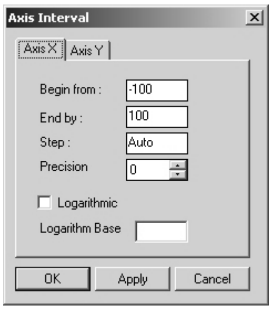
Button	***Function***
	storing as a graphic file
	opening the print dialog
	print preview

Changing chart properties

Button	***Function***
	selecting the chart type (e.g. x-y-chart or bar chart)
	selecting the color palette
	show/hide legend
	toggle 3D-view on/off
	tools for remarks and tags

Scaling

Click on the button  in order to change the scaling. The following dialog box opens:

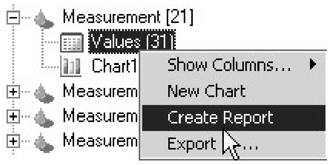


- Select one of the tabs "Axis X" or "Axis Y" to change the scaling for the corresponding axis.
- Enter a start value under "Begin from" and an end value under "End by".
- Enter the required distance between the tick marks under „Step".
- If required, select a logarithmic scaling and enter the base for the logarithm.

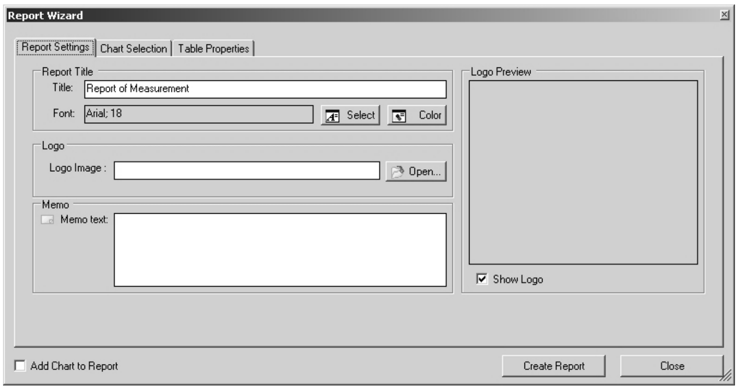
8.2.5 Creating a report

Special report options are available for the SFE calculations - →p. 93.

A comprehensive report can be printed out for each measurement by opening the context menu of the measurement or value entry in the database structure tree and selecting the option “Create Report”. A dialog opens for selecting the report options.



Report Settings



Edit the title of the report. If required, select another font and color for the title. If required, select a logo image (BMP format) using the “Open” button and select the option “Show Logo”

Under “Add Chart to Report” you can decide whether a plot is to be added.

Remarks (“Memo”) can be entered further down.

Chart Selections

To add a chart to the report you can either select a previously created chart (→p. 86) or create a new one. However, in the second case only a standard chart will be created; it is not possible to use the layout options for the chart.

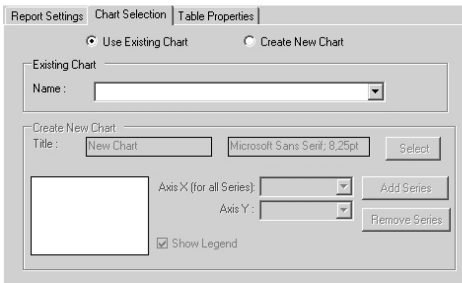


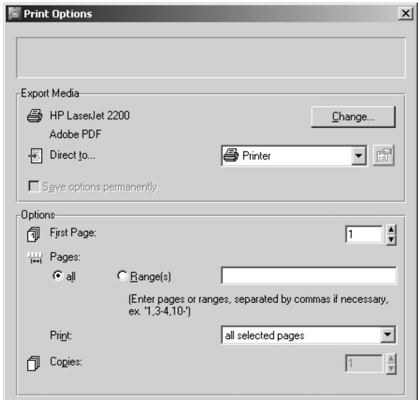
Table Properties

The quantities to be shown in the report’s table are compiled under „Table Properties“. The procedure is the same as for the „Values“ (→p. 85). In addition, you can select the quantity use for sorting the table under „Sort Table by“.

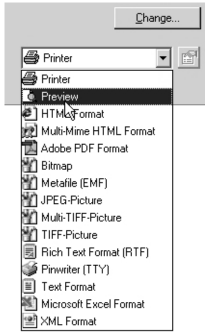
Printing and conversion options for reports

When all the settings have been made, click on [Create Report]. A dialog opens which provides you with a number of options for creating the report.

In the upper section you can define the output medium and format. The output setting is "Printer" – the report will be printed out on the standard printer. Alongside you can make a selection from a list of text-based (e.g. RTF, TXT, PDF), data-based (e.g. XLS), code-based (e.g. HTML, XML) and graphics output formats (e.g. JPG, BMP, TIF).



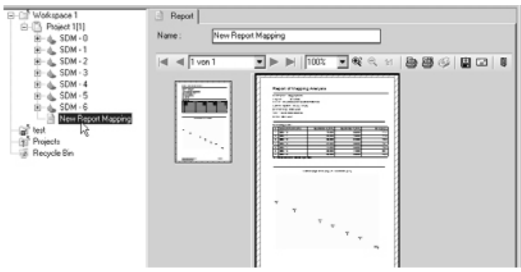
By selecting "Preview" you can see a preview.



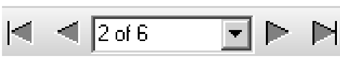
With some formats you can use the button to define further output options. For example it is possible to export just the data tables and not the diagrams when exporting to MS Excel.

Further down you can decide how many and which pages of the report are to be created: the first side to be shown is defined under "First Page", you can define a page region below. Finally you can decide whether the whole of the selected range ("all selected pages"), only the odd ("odd pages") or only the even ("even pages") pages are to be printed.

You should use the preview function (Preview) to make an assessment (see page margin). For reports of evaluations which are saved in the project you will additionally receive such a preview when the report is selected.



The symbol bar above the report provides you with the following possibilities:

	leaf through report
	zoom factor / zoom tools / original size
	print current page / print whole report
	save the report in various formats / send as e-mail

You can alter the print options in the context menu of the printer symbols .

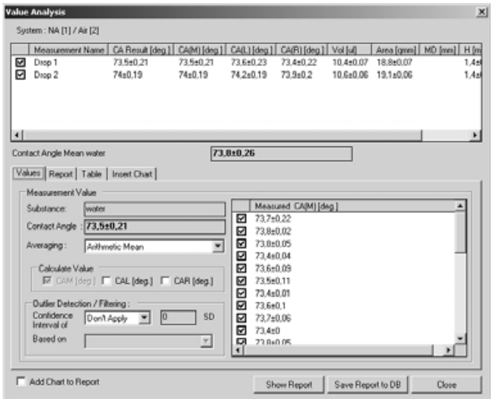
9 Evaluations

Various evaluations can be called up from the context menu of a project. This section covers the calculation of the mean value for several drops ("Value Analysis") and the calculation of the surface free energy ("Calculate SFE" →see p. 92). The evaluation of a mapping measurement is described in Section 10.3.

9.1 Contact angles of several drops ("Value Analysis")

Measurements on several drops of the same liquid can be evaluated in common with "Value Analysis". "Value Analysis" is accessed via the context menu of a project. It is possible:

- to calculate mean values for several drops.
- to statistically eliminate outliers.
- to summarize mean values and charts in a report.



The upper section lists all the measurements in the project; the measurements to be included in the evaluation can be selected by setting / removing the ticks. In the lower section of the dialog you can select whether a chart drawn up for the evaluation is to be added to the report ("Add Chart to report"). You can also view the report ("Show Report") and make sure that it is saved in the database together with the project ("Save Report to DB".

„Values"

Under "Values" you can define further evaluation options. The list to the right shows the measured values of the measurement marked above; here you can also exclude individual points from the evaluation. The meaning of the statistical options to the left corresponds to that of the "Statistics Settings" in the MT definition (→ p. 67).

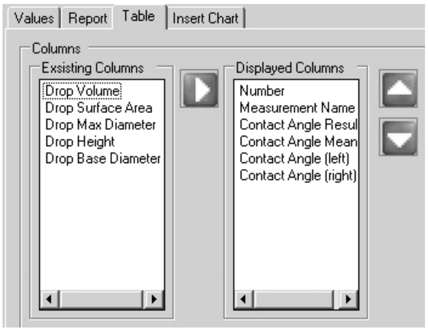
„Report"

The options for creating the report of an evaluation correspond to those of a single measurement (→ see p. 88).

„Table“

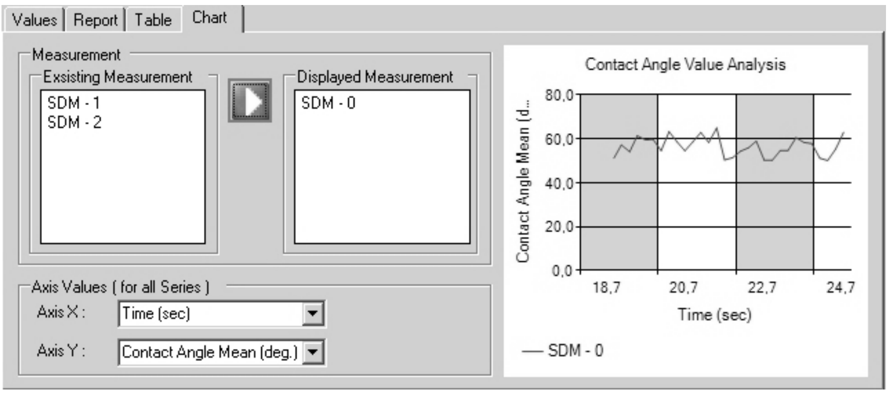
The measured quantities mentioned in the report are listed under “Table”.

The quantities not listed in the table are shown on the left, those that have been selected on the right. In order to edit the list of quantities to be shown select the corresponding line and click on the arrow button  or  to move the corresponding quantity from one list to the other. You can use the vertical arrow buttons to alter the sequence of the columns shown in the table.



„Insert Chart“

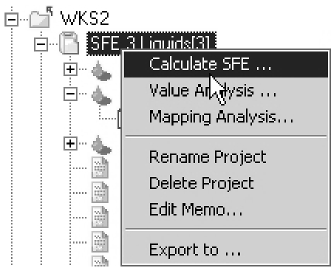
Here you can decide which measurements in the project are to be shown in a common chart in the report. The “Displayed” list is assembled in the same way as that used for the table by using the  and  arrow buttons. Below you can assign the quantity to be plotted to the X-axis and Y-axis of the chart. A preview of the chart can be seen on the right.



☝ By double-clicking on the diagram area you can open the diagram in an additional window and edit it.

9.2 Calculating the surface free energy

The surface free energy of a solid is obtained by measuring its contact angle with one or more liquids. The corresponding project is selected from the database. The command "Calculate SFE" opens a wizard for calculating the surface free energy.

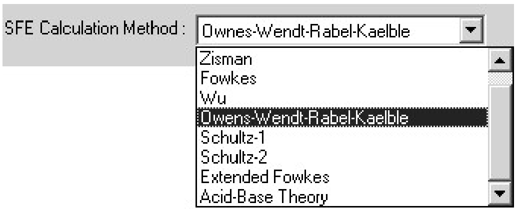


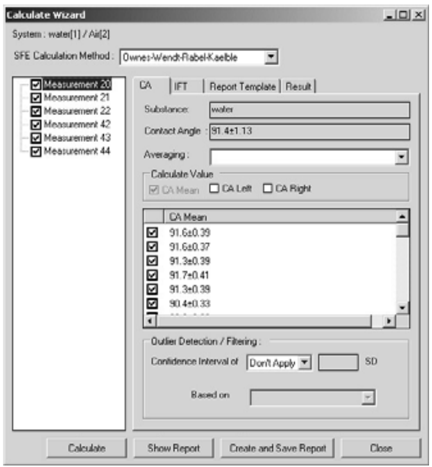
More details about SFE methods are given in Section 0 (Theory)

Selecting the measurements and method

On the left-hand side the measurements to be used for calculation are selected.

In the drop down menu above the desired SFE calculation method is selected.



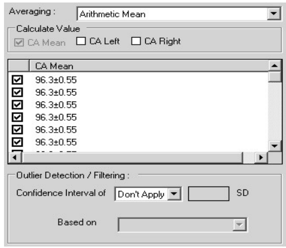


Method	Min. number of liquids
Equation of State (EOS)	1
Zisman	2
Fowkes	2 with pol/disp. data
Wu	2 with pol/disp. data
Ow/We/Ra/Kae	2 with pol/disp. data
Schultz-1	2 drops liquid + one surrounding phase
Schultz-2	1 drop liquid + 2 surrounding phases
Ext. Fowkes	3 with HH bridge data
Acid-base	2 with acid-base data

The more liquids you use, the more reliable the result.

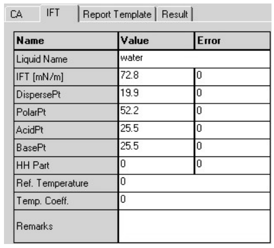
Mean values

Mean values are used for calculating the SFE. DSA3 does not use the mean values from the Results-Explorer, but calculates them from the settings made here. However, the way that they are used is the same (→p. 68).



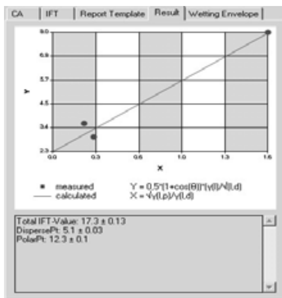
IFT

The physical and chemical data of the liquids used is listed on the "IFT" tab. This data is used for the calculation.
You can edit the liquid data here to use other values (e.g. from another literature source) for the calculation.



Result

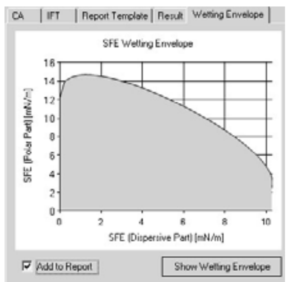
When you click on the Calculate button the calculation will be carried out and the result appears on the "Result" tab. Some calculations can be shown graphically; in such cases a plot will be shown in the upper part of the display. The result is shown in writing in the lower part.



Wetting Envelope

Some methods permit the presentation of the wetting envelope, which describes the wetting behavior of the solid. Initially the tab is empty; the wetting envelope can then be shown by clicking on Show Wetting Envelope.
The presentation shows a plot of the polar fraction against the disperse fraction of the surface tension. Liquids within the envelope completely wet the solid.

More details are given in section 0 (Theory)



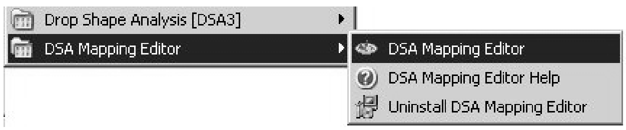
With the option "Add to Report" you can decide whether the wetting envelope plot is to be added to the report of the measurement.

10 Sample mapping

The DSA3 mapping is used to place virtual drops on a virtual sample, save the corresponding positions and use this so-called map for an actual sample onto which the mapped drops are positioned automatically. Thus, contact angles can be measured referring to the drop positions on a sample.

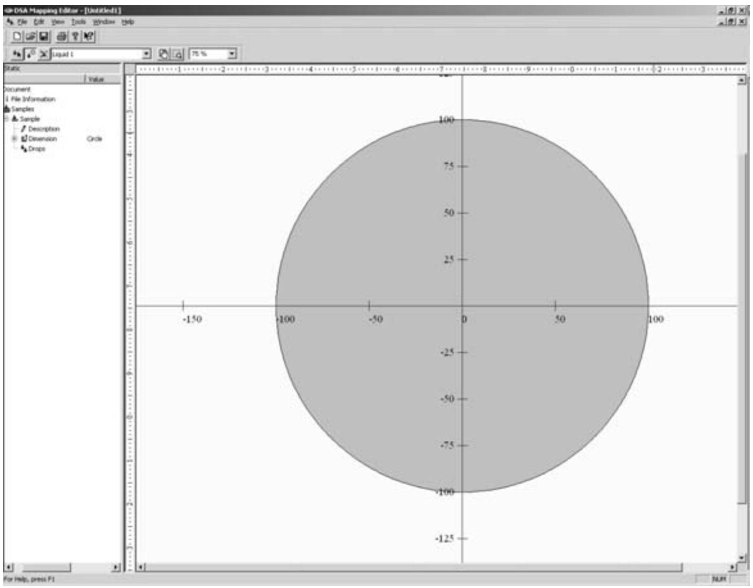
10.1 Defining a map: the DSA Mapping Editor

The DSA Mapping Editor is a stand-alone program which can be opened from the Windows start menu.



10.1.1 User interface

At the start of the program a circular standard map with a radius of 100 mm is displayed.

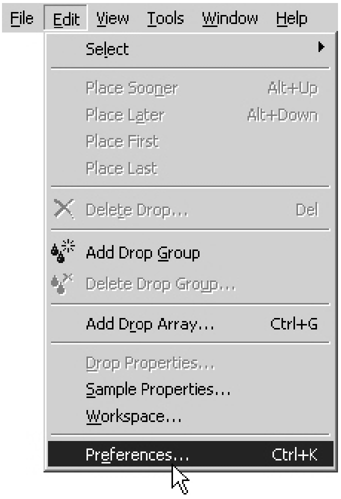


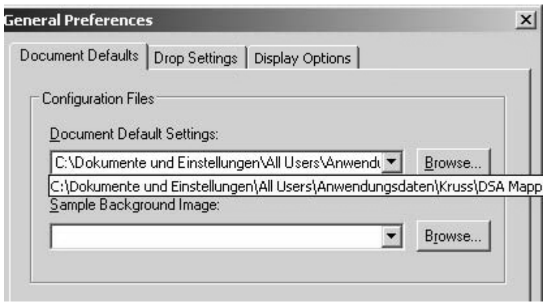
The view on the left side contains sample information and will later show data for all virtual drops placed on the map. The symbol bar contains icons that are used for (virtual) liquid selection, drop placement, viewing and data administration.

10.1.2 Switching between round and rectangular samples

The basic settings for the Mapping Editor are stored in the XML-file “Defaultsdisk.xml”, which is called up automatically at the start of the program. If you wish to use a rectangular sample template instead of the round one then proceed as follows:

1. Select the menu item “Edit”→“Preferences” and the “Document Defaults” tab. Move the mouse cursor over the input field “Document Default Settings” to read off the path for the XML-file.





2. Note down this path and search for the corresponding folder with “Browse”.

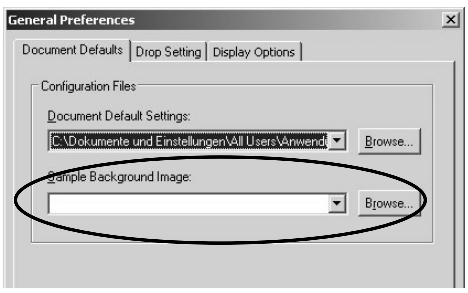
3. Instead of the file “Defaultsdisk.xml” select the file “Defaultsrect.xml”.

4. Close the Mapping Editor and restart it. A rectangular sample will now appear on the user interface.

☝ On →p. 107 a description of how you can selectively alter the Default XML-files is given. You should only make alterations when you are completely familiar with the meanings of the parameters. We also strongly advise you to make a backup copy of the original before you make any alterations.

10.1.3 Image as map

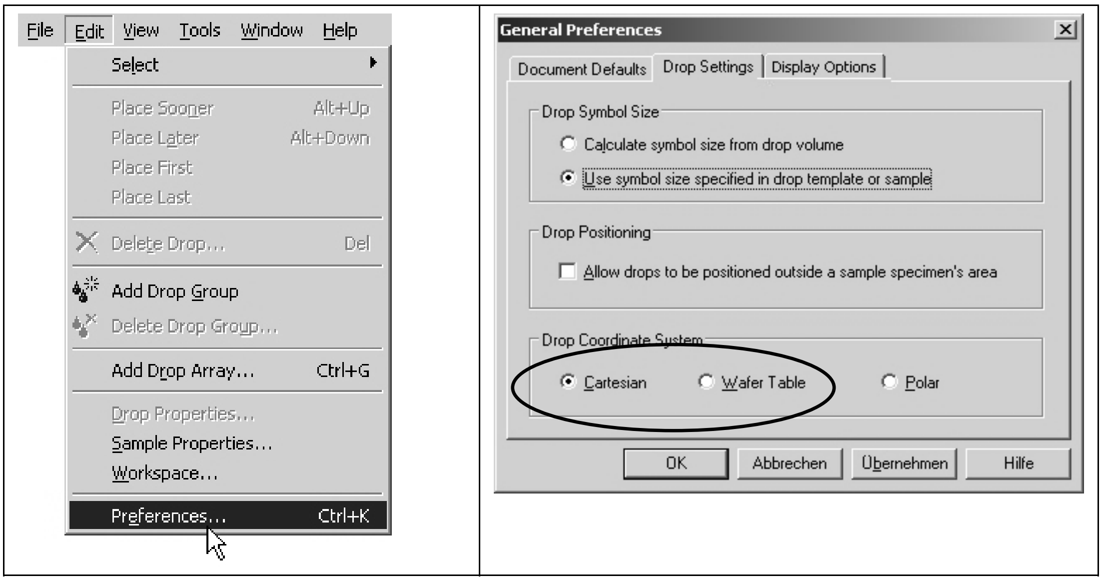
Under “Sample Background image” you can load any image (as a BMP-file) instead of a standard sample image and use it as a map.



10.1.4 Standard sample table / wafer table conversion

When drops are deposited coordinates are generated which are transferred to DSA3 for controlling the sample table. As the positions are addressed with either a standard sample table (X- and Y-axes) or with a wafer table, the memory format for the coordinates must be defined before the map is saved.

Select the menu item “Edit”→“Preferences” and the “Drop Settings” tab.



Use

- the setting “Cartesian” for a standard sample table (x/y-axes);
- the setting “Wafer Table“ for a wafer table.

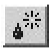
If the correct setting is not selected here then the sample positions will not be found correctly when the MT is carried out.

This conversion does not change anything on the user interface; the alterations only affect data storage and the communication with the DSA3 main program.

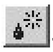
The option “Polar” for polar coordinates has not yet been implemented.

10.1.5 Setting drops

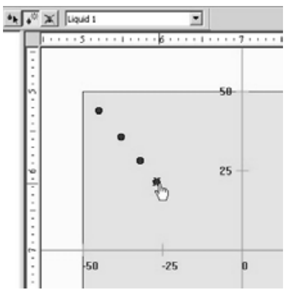
Toolbar icons

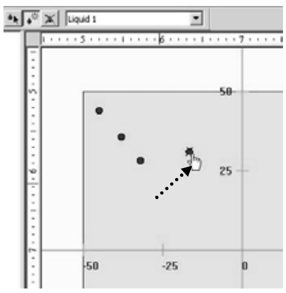
Icon	Function
	Select a virtual drop.
	Place virtual drops onto the map.
	Delete a virtual drop.
	Select the liquid for new virtual drops.

Drop positions

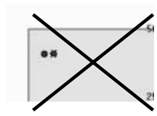
To place a drop on the virtual map, select a liquid and click on the icon . Then simply click on positions on the virtual sample to place virtual drops. Drops already placed on the map can be moved by drag-and-drop.

The actual test liquids have to be assigned to Liquids 1-8 in the DSA3 main program.



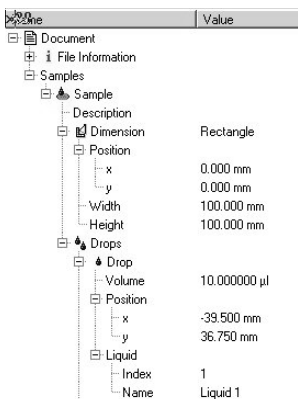


Do not set the drops too close on the same horizontal position because no proper image can be achieved when two drops lie in the optical axis.

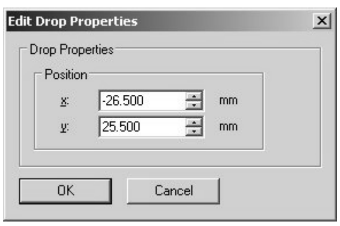


If such drop positions are required see the hints on page 104 .

In the DSA3 main program, the drops are dosed and measured in the sequence they have been placed onto the map. Information about the sample size and the drops (liquid and drop co-ordinates) is listed in the view on the left-hand side of the user interface.



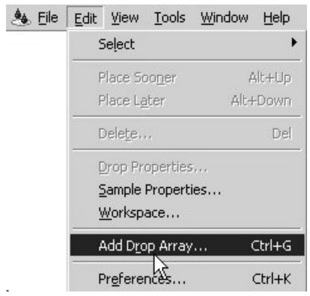
By clicking on a drop the marker jumps to the correcponding line in the drop list. By double-clicking on a drop an editing menu appears in which the co-ordinates of the drop can be set manually:



10.1.6 Creating an array

DSA3 does not recognize an array if single drops were placed on the virtual sample before *the array was created!*

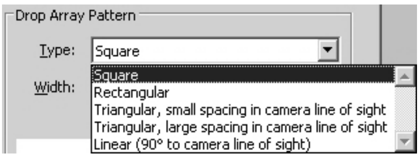
For one test liquid the drops can be arranged in an array with a defined pattern and distance between the single drops. The wizard for creating such an array is opened under "Edit"→"Add Drop Array…"



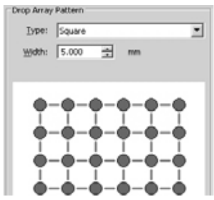
Presently, DSA3 can only carry out measurements with just one array. However, it is possible to add single drops *after* an array was created, even with other test liquids.

Pattern and distance between drops

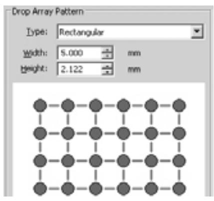
Several arrangements of an array are listed in the drop-down list box „Type":



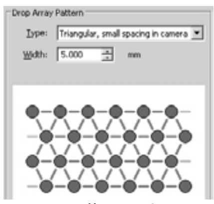
Square: Neighbouring drops form squares.



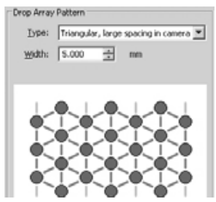
Rectangular: Neighbouring drops form rectangles (different distance in vertical ("Height") and vertical ("Width") direction).



Triangular, small/ large spacing in camera line of sight: Neighbouring drops form equilateral triangles. The distance between drops in x-direction (camera view) can be small or large.



„small spacing"



„large spacing"

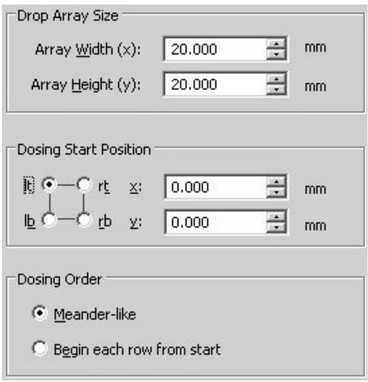
Linear: A Single line of drops is placed in y-direction (90° to camera view).

Array size and position and dosing order

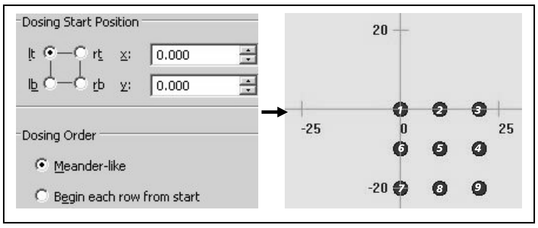
The size of the array is set in the upper two lines for x and y directions. The array cannot excess the sample limits.

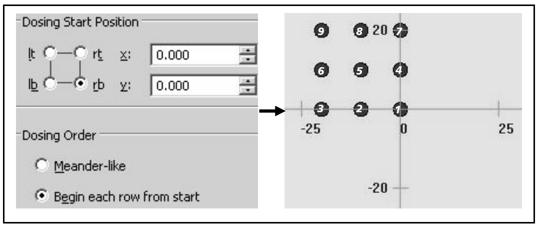
A starting point for dosing and the position of the array in relation to this point is set under "dosing start position".

The dosing of the drops can either be performed meander-like or with each row starting at the same x-Position ("each row from start").



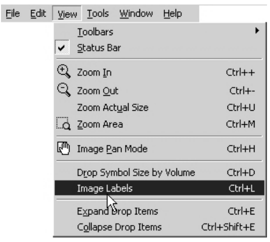
To avoid that remaining drops disturb further image evaluations it is a good idea to set the "Start Position" to the right and the "Dosing Order" to "each row from start".





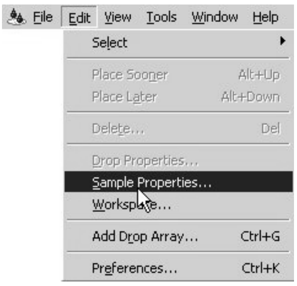
10.1.7 Displaying the drop number on the map

The run number of the drops can be displayed on the map. Select the menu item „View"→„Image Labels"

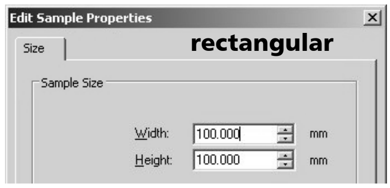


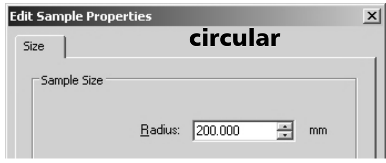
10.1.8 Changing the sample size

Select the menu item "Edit"→"Sample properties".



Set the required size (height/width or radius). If the size exeeds the range of the DSA100 y- and z-axes take care not to put virtual drops on places that cannot be reached by the axes.



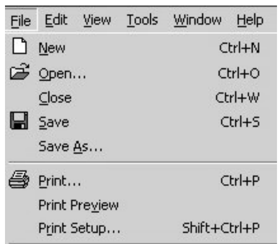


Sample position and size can only be changed when no drop is placed on the sample.

10.1.9 Loading/storing/printing maps

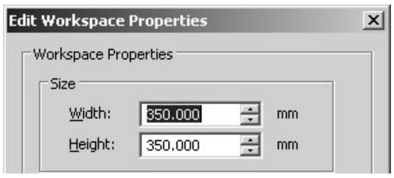
When drop properties are changed in the "defaults.xml" file(see page 107) older maps can contain drop data (size, liquid name, color) that do not correspond with the new defaults!

Under the menu item "File" maps and their corresponding virtual drops are stored and loaded. The map can also be printed out.
For these functions, the corresponding icons in the toolbar can also be used.

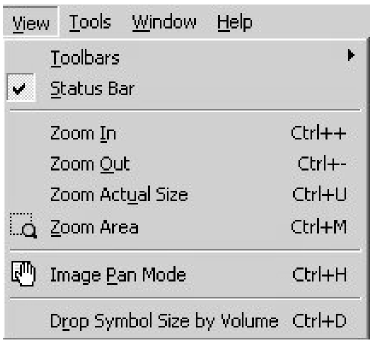


10.1.10 Changing the workspace area

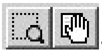
The size of the workspace can also be adjusted. Typically, these values refer to the actual range of the x- and y-axis of the DSA100.



10.1.11 Viewing options for the user interface



Viewing preferences can be set under the menu item "View". Toolbars and the status bar can be hidden or revealed. The sample and its drop positions can be zoomed in and out and switched back to actual size.

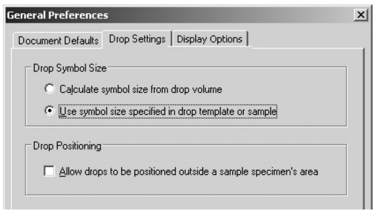
For "Zoom Area" and "Image Pan Mode" there are also icons in the toolbar: . With zoom area a rectangular area is set with drag-and-drop to which the zoom is adjusted. With pan mode the visible area can me moved.

The option "Drop Symbol Size by Volume" means that the size of the virtual drop is adjusted to the drop volume that is set in the default file "defaults.xml". This function helps to estimate how close to each other the drops can be set; however, the actual drop size depends on the contact angle and cannot be calculated exactly.

The volume set in the file "defaults.xml" and shown in the drop list of the mapping editor serves only to estimate the size of virtual drops and contains no information about the actual volume that is dosed with DSA3. The actual volume is set when the corresponding SDM is defined.

10.1.12 "Drop Settings"

Under "Edit"→ "General preferences"→ "Drop Settings" options for drop positioning and display are set.

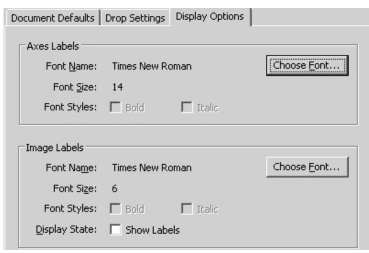


The option "drop symbol size" corresponds with the setting "Drop Symbol Size by Volume" in the "View"-Options.

The option "Drop positioning" makes it possible to place drops outside of the virtual sample.

10.1.13 "Display Options"

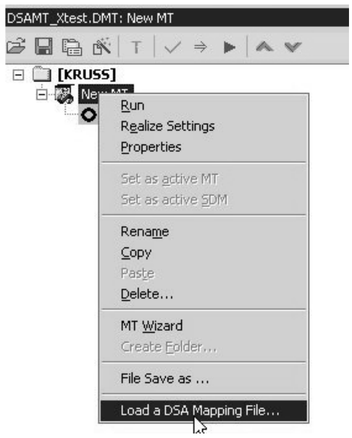
Under „Edit"→ "General preferences"→ "Display Options" the fonts and font sizes used for the "Axes Labels" and the drop numbers ("Image Labels")can be set. Click on „Choose Font" and select the font and font size for the selected element.



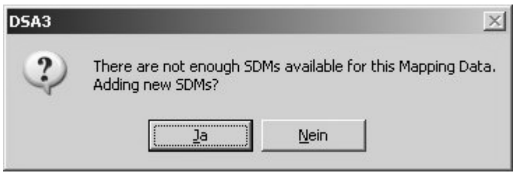
10.2 Using a mapping file for an MT

10.2.1 Load a mapping file

Since the z-Position cannot be programmed the mapping can’t be used for samples with uneven surfaces!

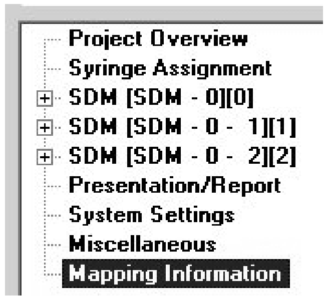


To load a mapping file to be used for an MT, set the MT as active, right-click on the MT and select the item “Load a DSA Mapping File…” from the context menu. Each virtual drop liquid used for the map corresponds to an SDM. If the number of liquids exeeds the number of SDMs in the current MT the required SDMs are created automatically:



10.2.2 Viewing Mapping properties

When using the Mapping tool, an SDM is not anymore a “single drop measurement". All mapped drops that were placed with the same virtual liquid are measured with one and the same SDM.



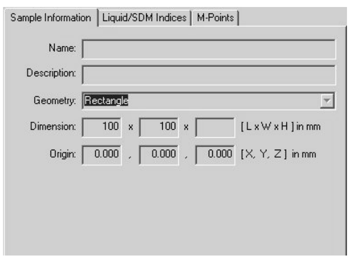
The new SDMs are now visible in the MT. Also, the new item “Mapping Information” appears in the list of MT settings.

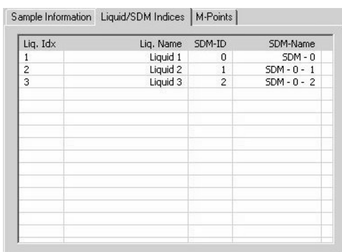
The data of the loaded mapping file is listed in three tab sheets:

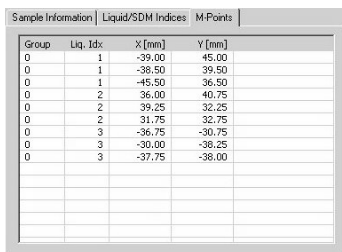
1.”Sample Information” containing size and position (referring to the origin of the map’s workspace).

2. “Liquid/SDM Indices” where the correspondance between the liquids used for the maps and the referring SDMs is shown.

3. “M-Points” displaying the x and y coordinates of each virtual drop.







10.2.3 Preparing the MT and the SDMs for measurement

Switch off the auto-delivery function when using the mapping function.

With the exception of the table position which is controlled by the mapping, all properties of the SDMs can be selected at will.

Assigning drop liquids

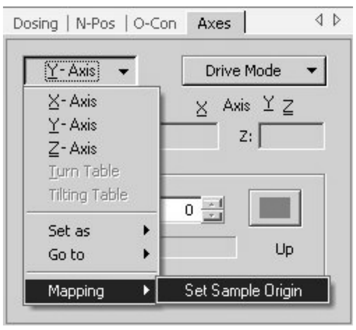
In most cases the only difference between the SDMs will be in the drop liquids used for them. In this case, the following steps are necessary:

1. The test liquids must be assigned to the syringes as described in section 6.3.
2. The syringe (drop phase) to be used for each SDM must be assigned to it as described in section 6.5.

Programming SDMs for a mapping

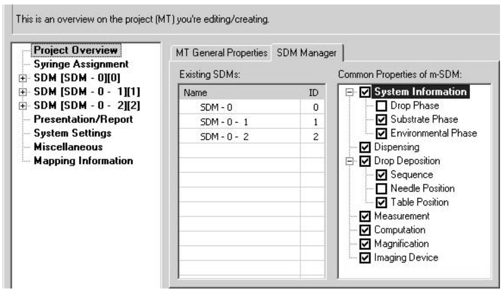
We recommend the following sequence:

1. Define all measurement parameters ("Measurement", "Computation" etc.) for the first SDM.
2. Place the sample on the sample table according to the position it had in the mapping file; the center of the sample table should correspond with the point 0/0 of the map.
3. Move the z-axis and the needle that is used for the first SDM to the correct height position for drop dosing. Store the needle position as "Deposition position" (see section 6.9).
4. Move the x- and y- axis so that the needle is exactly above the position which corresponds to 0-Position of the map. Define this axis setting as "Sample Origin" with the help of the CPanel:

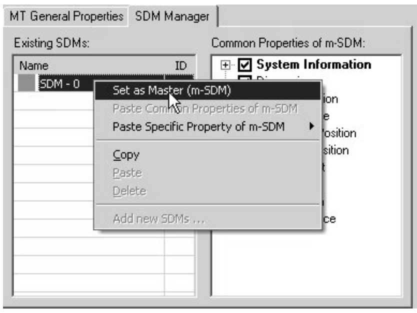


5. Set zoom, focus and illumination to optimal values for the first SDM.

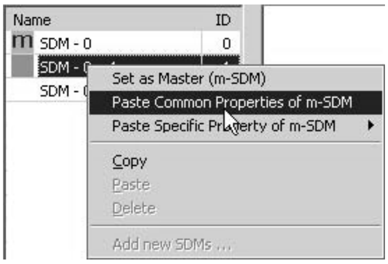
6. Usually, the parameters of this first SDM can be used for all others. Select the "SDM Manager" and set ticks for all parameters that the SDMs shall have in common. Leave out "Needle Position" and "Drop Phase".



7. Define the first SDM as "Master-SDM".



8. Copy the "Common Properties" from this Master-SDM to the other SDMs.



9. Define the "Deposition-Positions" of the needle for all other liquids / SDMs.

This is just the procedure for the standard use of the mapping function. Other applications are possible. For example, the different SDMs do not have to use different liquids, it is also possible to use them for different measurement parameters for one and the same liquid.

A standard application is to use one "liquid" of the mapping to suck drops from the sample. Place virtual drops of this "liquid" (by drag and drop) exactly on the positions of the drops to be removed. Use an empty syringe for the corresponding SDM and set the dosing volume to a negative value.

10.2.4 Starting a mapping measurement

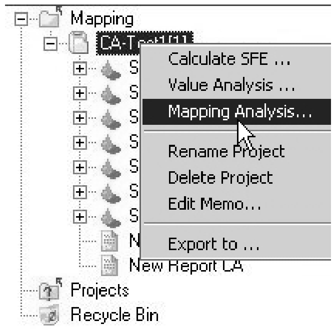
The mapping measurement is started with the icon  in the toolbar. The drops are dosed on the sample and measured in the order they were set when programming the mapping.

Once the mapping measurement runs properly it can be used for all samples of the same size. Samples that differ in height can be measured by adjusting the sample origin for each change of the sample.

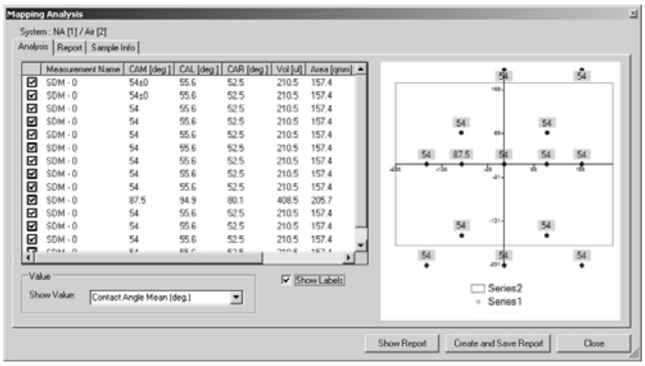
A running mapping measurement can be terminated with the ESC-key.

10.3 Evaluating a mapping measurement

When the mapping measurement is finished, its results are transferred to the database in the same way as usual measurements. The referring project can be evaluated by clicking it with the right mouse button and selecting the option “Mapping Analysis”.

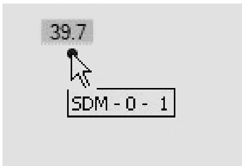


The evaluation shows a plot to which the drop positions are assigned.



Display options

- By setting or removing ticks in the table drops can be selected for the display. The drops appear in a certain colour for each liquid used in the mapping measurement.
- The dots representing the drop positions are labelled if the option "Show Labels" is selected. The quantity to be displayed is selected under "Show Value".
- By double-clicking the graph it can be displayed in a separate window.
- By clicking on a dot in the diagram the corresponding line in the table is indicated.
- The smarttag of a dot shows the name of the SDM, the smarttag of a label shows the liquid used for the measurement.



10.4 Settings in “Defaultsrect.xml” and „Defaultsdisk.xml“

The following image shows the parameters in the standard XML files for default settings and their meaning.

```
<?xml version="1.0" standalone="yes"?>
  <DSAMapEd>
    <DefaultWorkspace>
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rectangular

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circular

Save the file after making the alterations. The alterations will not be used in the running program, but only after the next program start.

11 Theory

In this section we first provide an introduction to the model considerations upon which interfacial tension is based (Section 11.1). This is followed by an explanation of the relationship between the contact angle and the surface energy of a solid upon which the individual methods for calculating the surface energy are based (Section 11.2). In addition, various methods of measuring the contact angle are described and an introduction is given to the theoretical background of the methods used in the DSA1 program for calculating the contact angle from the video images of sessile drops (Section 11.3). A further section deals with the theory of surface tension measurements using the images of pendant drops (Section 0).

11.1 Model considerations concerning interfacial tension

DUPRÉ defined the **work of cohesion** W_{ii} as the work done in dividing a homogeneous liquid per parting surface produced. As during division two individual parting surfaces 2A are produced, W_{ii} can be calculated from the surface tension σ (which is defined as the work per surface difference) according to the following equation:

$$W_{ii} = 2\sigma$$ Equation 1

If a liquid column consists of 2 immiscible liquids then, when the column is separated, 2 new parting surfaces are formed at the interface and the boundary surface disappears. Therefore, according to DUPRÉ, the following relationship exists for the **work of adhesion** :

$$W_{ij} = \sigma_i + \sigma_j - \gamma_{ij}$$ Equation 2,

where γ_{ij} represents the interfacial tension between the two phases.

ANTONOW has calculated the interfacial tension from the difference between the surface tensions of the individual phases:

$$\gamma_{12} = |\sigma_1 - \sigma_2|$$ Equation 3

with the surface tensions σ_1, σ_2 of the individual components (this observation also forms the basis for the method according to ZISMAN described below (see Section 11.2.1). However ANTONOW's approach proved to be an approximation that was not sufficiently accurate.

GOOD and GIRIFALCO describe the work of cohesion as being dependent on the geometric mean of the interactive energies between the particles of the two individual phases:

$$W_{12} = 2\Phi\sqrt{\sigma_1 \cdot \sigma_2} \quad \text{Equation 4.}$$

By combining Equations 2 and 4 and transposition for $\gamma_{12}$the following relationship is obtained.

$$\gamma_{12} = \sigma_1 + \sigma_2 - 2\Phi\sqrt{\sigma_1 \cdot \sigma_2}\gamma \quad \text{Equation 5}$$

The interaction parameter Φ introduced here is a complex function of molecular quantities and initially could only be determined empirically.

FOWKES was the first to prepare the way for the calculation of interfacial tensions from surface tension data. He specified the interactions represented by the parameter Φ by assuming that only the same types of interactions could occur between the phases. For example, according to this only a nonpolar substance, i.e. a **purely disperse** interactive substance, can interact with the disperse fractions of the surrounding second phase:

$$\gamma_{12} = \sigma_1 + \sigma_2 - 2\sqrt{\sigma_1^D \cdot \sigma_2^D} \quad \text{Equation 6}$$

The disperse character of the interactions is expressed by the index D.

While dispersion forces exist in all atoms and molecules, polar forces are only found in certain molecules. Polar forces have their source in the differing electronegativity of different atoms in the same molecule. For polar liquids OWENS, WENDT, RABEL and KAELBLE (1969) assumed that there was a **polar fraction of the surface tension**. According to their model, the surface tension was the sum of the disperse and polar fractions:

$$\sigma = \sigma^D + \sigma^P \quad \text{Equation 7.}$$

For the interfacial tension between two phases with polar fractions the following equation (8) is obtained as an extension of Equation 6:

$$\gamma_{12} = \sigma_1 + \sigma_2 - 2(\sqrt{\sigma_1^D \cdot \sigma_2^D} + \sqrt{\sigma_1^P \cdot \sigma_2^P}) \quad \text{Equation 8.}$$

In the "Extended FOWKES" method a further interactive fraction is also differentiated; the interactions caused by **hydrogen bondings**:

$$\sigma = \sigma^D + \sigma^P + \sigma^H$$ Equation 9

with the corresponding extension of Equation 8 for the calculation of the interfacial tension by a further square root term:

$$\gamma_{12} = \sigma_1 + \sigma_2 - 2(\sqrt{\sigma_1^D \cdot \sigma_2^D} + \sqrt{\sigma_1^P \cdot \sigma_2^P} + \sqrt{\sigma_1^H \cdot \sigma_2^H})$$ Eq. 10.

equations 6, 8 and 10 use the **geometric mean** of the particular surface tension components of the individual phases. They produce satisfactory results throughout a wide range of surface energies.

The model according to OSS and GOOD is also based on the geometric mean, but the polar fraction is described with the help of the **Acid-Base-Model** according to LEWIS. The polar fraction is divided into an acid part σ^+ and a base part σ^-; this leads to the following equation:

$$\gamma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^+ \cdot \sigma_l^-} + \sqrt{\sigma_s^- \cdot \sigma_l^+})$$ Gl. 11.

For low-energy systems (surface energies up to ≈35mN/m) the method according to WU can be used as an alternative. WU uses the **harmonic mean** instead of the geometric mean and limits it to the disperse and polar fractions.

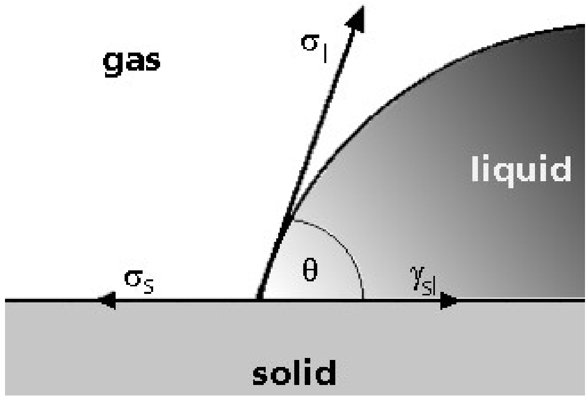
$$\gamma_{12} = \sigma_1 + \sigma_2 - 4(\frac{\sigma_1^D \cdot \sigma_2^D}{\sigma_1^D + \sigma_2^D} + \frac{\sigma_1^P \cdot \sigma_2^P}{\sigma_1^P + \sigma_2^P})$$ Equation 12

In this way WU obtained more accurate results for low energy systems. However, the use of the harmonic mean is not suitable for high-energy materials (e.g. mercury, glass, metal oxides, graphite, polar polymers).

With the aid of the methods described here it is possible to calculate the interfacial tensions between liquids, provided that their surface tensions and disperse and polar fractions (and, if applicable, their hydrogen bridge fractions) are known. In addition the surface energies of solids can also be calculated. A requirement for this is the knowledge of the **contact angles** of the corresponding liquids during phase contact with the solid surface.

11.2 Contact angle and surface energy

In 1805 YOUNG had already formulated a relationship between the interfacial tensions at a point on a 3-phase contact line.



Indices s and l stand for "solid" and "liquid"; the symbols σ_s and σ_l describe the surface tension components of the two phases; symbol γ_{sl} represents the interfacial tension between the two phases, and θ stands for the contact angle corresponding to the angle between vectors σ_l and γ_{sl}. YOUNG formulated the following relationship between these quantities:

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta$$ Equation 13.

The methods implemented in the DSA1 program allow the determination of the surface energy of solids from contact angle data. They are mainly based on combining various starting equations for γ_{sl} with the equation from YOUNG to obtain equations of state in which $\cos\theta$ represents a function of the phase surface tensions and, if applicable, the (polar and disperse) tension components $\sigma_{l,D}$, $\sigma_{l,P}$, $\sigma_{s,D}$ and $\sigma_{s,P}$. As liquids with known surface tension data and known polar and disperse fractions are used it is possible to include $\sigma_{l,D}$ and $\sigma_{l,P}$ in the equations. All methods assume that the interactions between the solid and the gas phase (or the liquid vapour phase) are so small as to be negligible. The methods are described in the following sections.

11.2.1 The ZISMAN method

In the ZISMAN method the surface energy of the solid is determined by using the **critical surface tension** (explained below) of the liquid. This method is based on a revised version of the ANTONOW method, it is implemented in the DSA1 program primarily for historical reasons and should not be used for routine measurements.

The method is based on the following consideration:

A liquid wets a solid completely when the work of cohesion for the formation of a liquid surface W_{ll} is smaller than the work of cohesion for the formation of the interface boundary W_{sl}. The difference between these two quantities is known as the spreading pressure $S_{l/s}$:

$$S_{l/s} = W_{sl} - W_{ll}$$ Equation 14.

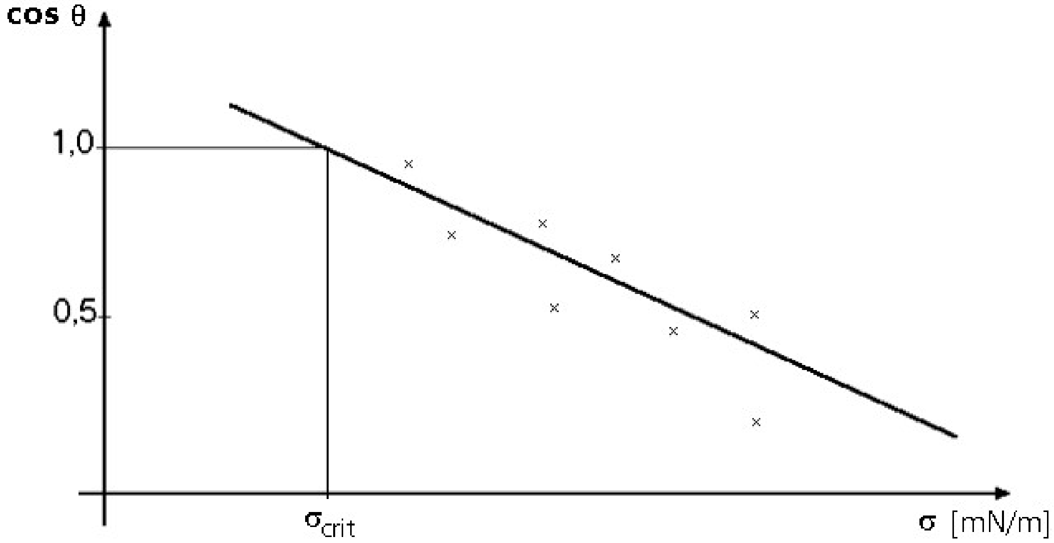
The solid will be wetted completely when the spreading pressure is positive; at a negative spreading pressure the solid will not be wetted completely.

In addition, the following relationship exists between the work of cohesion W_{sl}, the contact angle θ and the surface tension of the liquid:

$$W_{sl} = \sigma_l (\cos\theta + 1)$$ Equation 15

As the work of cohesion W_{ll} is defined as $2 \cdot \sigma_l$ according to DUPRÉ then, for a contact angle of 0° $(\cos\theta = 1)$ the work of cohesion will be the same as the work of adhesion; this results in a spreading pressure of 0. This means that the contact angle of 0° can be called the limiting angle for spreading (=complete wetting). Theoretically, a positive spreading pressure corresponds with negative contact angles which cannot be measured in practice.

The method according to ZISMAN uses this relationship by plotting $\cos\theta$ against the surface tension for various liquids and extrapolating the compensation curve to $\cos\theta = 1$. The corresponding value for the surface tension is known as the critical surface tension σ_{crit}.



ZISMAN equates this value with the surface energy of the solid σ_s. Setting up a linear relationship between $\cos\theta$ and the surface tension σ_l is based on the now outdated assumption of ANTONOW that the interfacial tension is determined by the difference between the surface tensions. In fact this linear relationship only applies when the relationship between the disperse and polar interactions is the same between the solid and the liquid. This practically only occurs when a purely disperse interactive solid and liquid are involved; i.e. only under exceptional circumstances. This means that other methods should normally be used for determining the surface energy.

11.2.2 Equation of state

The equation of state was obtained during the search for a method of determining the surface energy of a solid from a single contact angle measurement by using a liquid with known surface tension.

Starting with the equation of Young

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \qquad \text{Equation 16}$$

it can be seen that a second equation is required which also describes the surface energy of the solid as a function of the interfacial tension solid/liquid and the surface tension of the liquid:

$$\sigma_s = f(\gamma_{sl}, \sigma_l) \qquad \text{Equation 17}$$

From thermodynamic considerations it was first demonstrated that such an equation valid for all systems must exist. By using an enormous volume of contact angle data the required equation of state was determined empirically:

$$\gamma_{sl} = \sigma_l + \sigma_s - 2\sqrt{\sigma_l \cdot \sigma_s} \cdot e^{-\beta(\sigma_l - \sigma_s)^2} \qquad \text{Equation 18}$$

The value 0.0001247 was determined for the constant β in the exponent. If the equation of state is inserted in Young's equation then a new equation is obtained which allows the calculation of the surface tension of the solid σ_s from a single contact angle if the surface tension σ_l is known:

$$\cos\theta = -1 + 2\sqrt{\frac{\sigma_s}{\sigma_l}} \cdot e^{-\beta(\sigma_l - \sigma_s)^2} \qquad \text{Equation 19}$$

In the calculation of the surface energy with the help of the equation of state the type of interactions which lead to the formation of the interfacial tensions (polar or disperse interactions) are not taken into account. However, the assumption that the knowledge of the surface tension of the liquid alone is sufficient has been disproved by experiments in which the contact angles of liquids with similar high surface tensions and differing fractions of polar interactions were measured. It appears that the disperse and polar fractions of the surface tensions must be taken into account; this means that the equation of state only provides useful results when only disperse interactions are present or when these are in the majority.

11.2.3 The method according to FOWKES

By using the FOWKES method the polar and disperse fractions of the surface free energy of a solid can be obtained. Strictly speaking this method is based on a combination of the knowledge of FOWKES on the one hand and that of OWENS, WENDT, RABEL and KAELBLE on the other, as FOWKES initially determined only the disperse fraction and the latter were the first to determine both the components of the surface energy. The difference between the FOWKES method used by KRÜSS and the OWENS, WENDT, RABEL and KAELBLE method is that in the **FOWKES method** the **disperse and the polar fractions are** determined in succession, i.e. **in two steps**, while in the OWENS, WENDT, RABEL and KAELBLE method both components are calculated by using a single linear regression.

The calculation steps described below are only intended to explain the methods. When calculating the surface energy according to FOWKES you do not have to proceed in several steps; when the calculation is carried out these steps are processed internally by the program. The same applies for the “Extended FOWKES” method described in Section 11.2.4.

11.2.3.1 Step 1: Determining the disperse fraction

In this first step the disperse fraction of the surface energy of the solid is calculated by making contact angle measurements with at least one purely disperse liquid.

By combination of the surface tension equation of FOWKES for the disperse fraction of the interactions

$$\gamma_{sl} = \sigma_s + \sigma_l - 2\sqrt{\sigma_s^D \cdot \sigma_l^D}$$ Equation 20

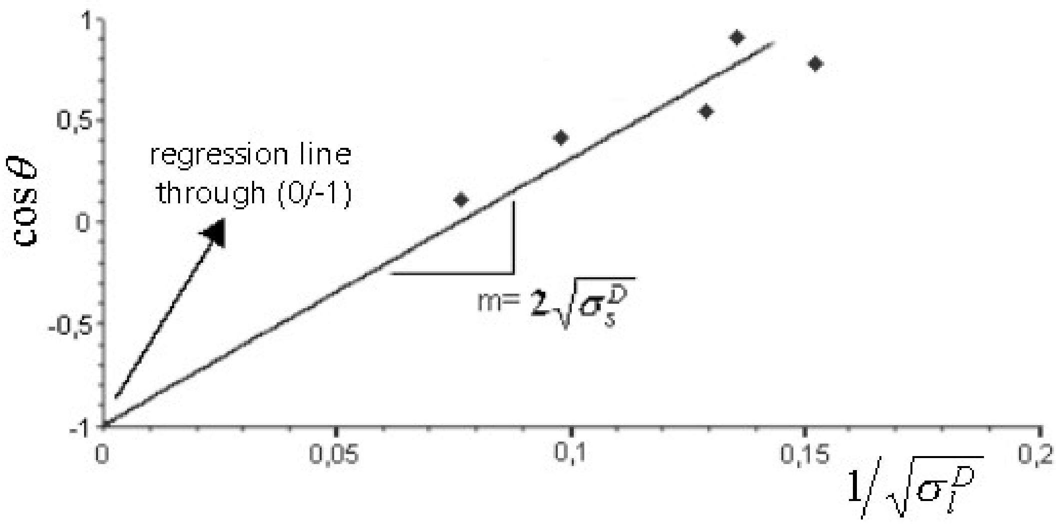
with the YOUNG equation (16) the following equation for the contact angle is obtained after transposition:

$$\cos\theta = 2\sqrt{\sigma_s^D} \cdot \frac{1}{\sqrt{\sigma_l^D}} - 1$$ Equation 21

and, based upon the general equation for a straight line,

$$y = mx + b$$ Equation 22

$\cos\theta$ is then plotted against the term $1/\sqrt{\sigma_l^D}$ and $2\sqrt{\sigma_s^D}$ can be determined from the slope m. The straight line must intercept the ordinate at the point defined as b=-1 (0/-1). As this point has been defined it is possible to determine the disperse fraction from a single contact angle: however, a linear regression with several purely disperse liquids is more accurate.



11.2.3.2 Step 2: Determining the polar fraction

For the 2nd step, the calculation of the polar fraction, equation 20 is extended by the polar fraction:

$$\gamma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P}) \qquad \text{Equation 23.}$$

It is also assumed that the work of adhesion is obtained by adding together the polar and disperse fractions:

$$W_{sl} = W_{sl}^D + W_{sl}^P \qquad \text{Equation 24}$$

and then as a third step YOUNG's equation

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \qquad \text{Equation 25}$$

is added to the equation of DUPRÉ

$$W_{sl} = \sigma_s + \sigma_l - \gamma_{sl} \qquad \text{Equation 26}$$

to obtain the following relationship for the work of adhesion:

$$W_{sl} = \sigma_l(\cos\theta + 1) \qquad \text{Equation 27}$$

Now all the components required for the calculation of the polar fraction of the surface energy have been assembled. A combination of equations 23, 24 and 27 produces

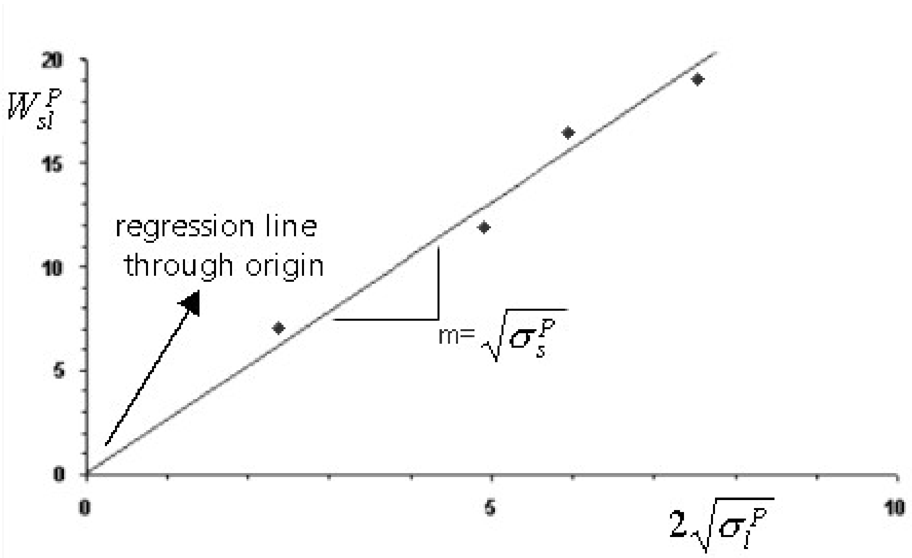
$$W_{sl}^P = \sigma_l(\cos\theta + 1) - 2\sqrt{\sigma_s^D \cdot \sigma_l^D} \qquad \text{Equation 28.}$$

Based upon this relationship the contact angles of liquids with known polar and disperse fractions are measured and W_{sl}^P is calculated for each liquid. In this case a single liquid with polar and disperse fractions would be sufficient, although the results would again be less reliable.

As according to Equation 23 the polar fraction of the work of adhesion is defined by the geometric mean of the polar fractions of the particular surface tensions

$$W_{sl}^P = 2\sqrt{\sigma_l^P} \cdot \sqrt{\sigma_s^P}$$ Equation 29,

then, by plotting W_{sl}^P against $2\sqrt{\sigma_l^P}$ and following this with a linear regression, the polar fraction of the surface energy of the solid can be determined from the slope. As in this case the ordinate intercept b is 0, the regression curve must pass through the origin (0;0).



11.2.4 The Extended FOWKES method

In the Extended FOWKES method the work of adhesion is not split up into just two fractions but into three: the **disperse** and **polar** fractions as well as the fraction W_{sl}^H resulting from the **hydrogen bridges**:

$$W_{sl} = W_{sl}^D + W_{sl}^P + W_{sl}^H$$ Equation 30.

The calculation of the surface energy accordingly is carried out in **three steps** instead of two.

As in the **first step** of the FOWKES method the disperse fraction of the surface energy of a solid is determined from the contact angle data of a purely disperse liquid.

In the **second step** liquids with known polar and disperse surface tension fractions are selected (σ_l^D and $\sigma_l^P > 0$) with a hydrogen bridge fraction σ_l^H of 0. In this way, as in the second step of the FOWKES method, the polar fraction of the surface free energy is first obtained with the aid of contact angle measurements (by subtracting the disperse fraction from the total work of adhesion).

$$W_{sl}^P = \sigma_l(\cos\theta + 1) - 2\sqrt{\sigma_s^D \sigma_l^D}$$ Equation 31.

The determination of the polar fraction of the surface free energy of the solid is carried out as in the FOWKES method.

In a **third step** work is again carried out in a similar manner for the calculation of the hydrogen bridge fraction. Contact angles of liquids with known polar, disperse and hydrogen bridge fractions (σ_l^H >0) of the surface tension are measured. By extending Equation 23 by the hydrogen bridge fraction we obtain

$$\gamma_{12} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P} + \sqrt{\sigma_s^H \cdot \sigma_l^H})$$ Eq. 32

As in Equation 28 the required fraction of the work of adhesion, i.e. the fraction W_{sl}^H resulting from the hydrogen bridges, can be calculated for each contact angle by subtracting the known fractions (by including the YOUNG Equation (25)):

$$W_{sl}^H = \sigma_l(\cos\theta + 1) - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P})$$ Equation 33.

Finally the hydrogen bridge fraction σ_s^H of the surface energy of the solid can now be determined as described in Step 2 of the FOWKES method. According to Equation 32 the following relationship applies to W_{sl}^H:

$$W_{sl}^H = 2\sqrt{\sigma_l^H} \cdot \sqrt{\sigma_s^H}$$ Equation 34.

If W_{sl}^H is plotted against $2\sqrt{\sigma_l^H}$ then $\sqrt{\sigma_s^H}$, i.e. the hydrogen bridge fraction of the surface energy of the solid, is obtained from the slope of the regression curve.

11.2.5 **The Owens, Wendt, Rabel and Kaelble method**

According to OWENS, WENDT, RABEL and KAELBLE the surface tension of each phase can be split up into a polar and a disperse fraction:

$$\sigma_l = \sigma_l^P + \sigma_l^D$$ Equation 35

$$\sigma_s = \sigma_s^P + \sigma_s^D$$ Equation 36.

The FOWKES method for calculating the surface energy has already been developed from this relationship. In contrast to the FOWKES method, in the OWENS, WENDT, RABEL and KAELBLE method the calculation of the surface energy of the solid takes place in a single step.

OWENS and WENDT took the equation for the surface tension

$$\gamma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P})$$ Equation 37

as their basis and combined it with the YOUNG equation

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta$$ Equation 38.

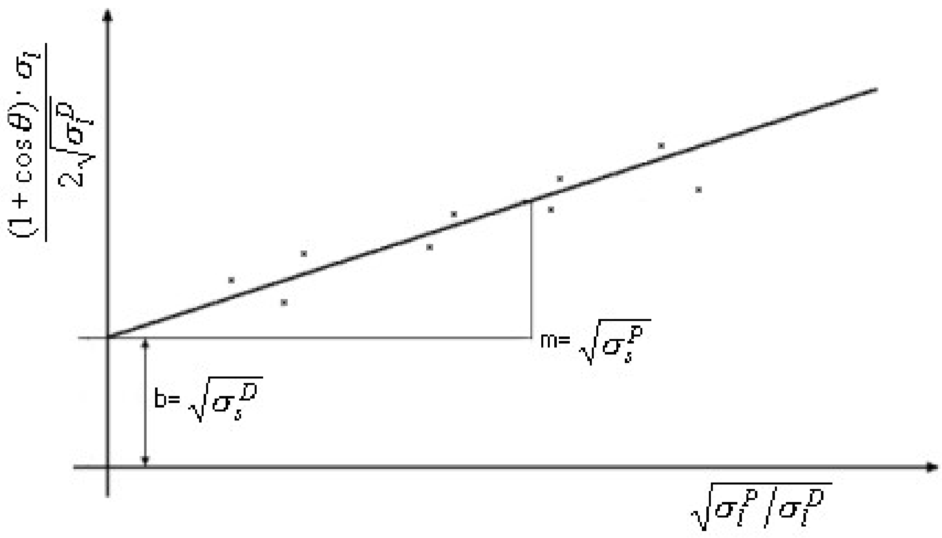
The two authors solved the equation system by using the contact angles of two liquids with known disperse and polar fractions of the surface tension. KAELBLE solved the equation for combinations of two liquids and calculated the mean values of the resulting values for the surface energy. RABEL made it possible to calculate the polar and disperse fractions of the surface energy with the aid of a single linear regression from the contact angle data of various liquids. He combined equations 37 and 38 and adapted the resulting equation by transposition to the general equation for a straight line

$$y = mx + b$$ Equation 39

The transposed equation is shown below:

$$\underbrace{\frac{(1+\cos\theta)\cdot\sigma_l}{2\sqrt{\sigma_l^D}}}_{y} = \underbrace{\sqrt{\sigma_s^P}}_{m}\underbrace{\sqrt{\frac{\sigma_l^P}{\sigma_l^D}}}_{x} + \underbrace{\sqrt{\sigma_s^D}}_{b}$$ Equation 40.

In a linear regression of the plot of y against x, σ_s^P is obtained from the square of the slope of the curve m and σ_s^D from the square of the ordinate intercept b.



11.2.6 The WU method

In his observations on interfacial tension WU also started with the polar and disperse fractions of the surface energy of the participating phases. However, in contrast to FOWKES and OWENS, WENDT, RABEL and KAELBLE, who used the geometric mean of the surface tensions in their calculations, WU used the **harmonic** mean. In this way he achieved more accurate results, in particular for high-energy systems.

At least two test liquids with known polar and disperse fractions are required for this method; at least one of the liquids must have a polar fraction >0.

WU's initial equation for the interfacial tension between a liquid and a solid phase is as follows:

$$\gamma_{12} = \sigma_l + \sigma_s - 4\left(\frac{\sigma_l^D \cdot \sigma_s^D}{\sigma_l^D + \sigma_s^D} + \frac{\sigma_l^P \cdot \sigma_s^P}{\sigma_l^P + \sigma_s^P}\right) \qquad \text{Equation 41.}$$

If YOUNG's equation is inserted in equation 41

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \qquad \text{Equation 42}$$

then the following relationship is obtained:

$$\sigma_l(\cos\theta + 1) - 4\left(\frac{\sigma_l^D \cdot \sigma_s^D}{\sigma_l^D + \sigma_s^D} + \frac{\sigma_l^P \cdot \sigma_s^P}{\sigma_l^P + \sigma_s^P}\right) = 0 \qquad \text{Equation 43.}$$

In order to determine the two required quantities σ_s^D and σ_s^P, WU determined the contact angles for each of two liquids on the solid surface and then, based on equation 43, he drew up an equation for each liquid. After a factor analysis the resulting equations were as follows:

$$(b_1 + c_1 - a_1)\sigma_s^D \sigma_s^P + c_1(b_1 - a_1)\sigma_s^D + b_1(c_1 - a_1)\sigma_s^P - a_1 b_1 c_1 = 0 \qquad \text{Eq. 44}$$

$$(b_2 + c_2 - a_2)\sigma_s^D \sigma_s^P + c_2(b_2 - a_2)\sigma_s^D + b_2(c_2 - a_2)\sigma_s^P - a_2 b_2 c_2 = 0 \qquad \text{Eq. 45}$$

The variables a_1, b_1, c_1 for the first liquid and a_2,b_2,c_2 for the second liquid express the following terms:

a_1	$\frac{1}{4}\sigma_{l,1}(\cos\theta_1 + 1)$
b_1	$\sigma_{l,1}^D$
c_1	$\sigma_{l,1}^P$
a_2	$\frac{1}{4}\sigma_{l,2}(\cos\theta_2 + 1)$
b_2	$\sigma_{l,2}^D$
c_2	$\sigma_{l,2}^P$

The solution of the equations produces the surface energy of the solid σ_s and its polar end disperse components σ_s^P and σ_s^D. However, the following point must be taken into consideration: as quadratic equations are involved this means that two solutions are obtained for both σ_s^P and σ_s^D; only one of these solutions describes the actual surface energy.

Although the equation system drawn up by WU can be solved with the contact angle data obtained with two liquids, as in other methods the selection of a larger number of test liquids increases the reliability of the measurements. As WU uses two equations for two liquids to calculate the surface energy, a part-result is obtained for each of the possible pairings of the test liquids.

For example:

The surface energy of a solid is to be determined by using the contact angles of 4 test liquids: water, diiodomethane, ethylene glycol and benzyl alcohol. The calculation is carried out for each of the six possible pairings:

	Liquid 1	**Liquid 2**
1st pair	water	diiodomethane
2nd pair	water	ethylene glycol
3rd pair	water	benzyl alcohol
4th pair	diiodomethane	ethylene glycol
5th pair	diiodomethane	benzyl alcohol
6th pair	ethylene glycol	benzyl alcohol

This means that the 4 test liquids supply 6 part-results; as described above, each of these results has two solutions. This means that the choice of the right solution must be made for each individual pair of liquids. The pairing of two purely disperse liquids ($\sigma_l^P = 0$) produces no solution for the equation system; they are not included in the calculation. The final result of the surface energy determination is the arithmetic mean of the selected part-results.

11.2.7 The SCHULTZ method

The method for calculating the surface energy according to SCHULTZ is only intended for use with high-energy solid surfaces. In the DSA1 program there are two methods implemented which are based on SCHULTZ: “SCHULTZ 1” and “SCHULTZ 2”. The theoretical requirements are the same for both methods; the difference lies in the test arrangement. As a result this section first described the theoretical principles and only then explains the differences between the two SCHULTZ methods.

11.2.7.1 Theoretical principles for the two SCHULTZ methods

High-energy solids are normally completely wetted by all liquids, so that their surface energy cannot be determined by using conventional contact angle measurements. In order to be able to investigate such systems at all the test arrangement must be altered: instead of being measured in air, the contact angle of a liquid drop (“drop phase”) on a solid is measured in a liquid phase (“bulk phase”).

The calculation of the surface energy assumes that the YOUNG equation also applies to a liquid/liquid/solid system:

$$\sigma_s = \gamma_{sl_{drop}} + \gamma_{ll\,drop/bulk} \cdot \cos\theta$$ Equation 46.

In this case $\gamma_{sl_{bulk}}$ represents the interfacial tension between the solid and the surrounding phase; $\gamma_{sl_{drop}}$ the interfacial tension between the solid and the drop phase; and $\gamma_{ll\,drop/bulk}$ the interfacial tension between the two liquids.

With the equations of FOWKES and OWENS, WENDT, RABEL and KAELBLE (Equation 37) adapted for a liquid/liquid/solid system, the following equations are obtained for the drop phase and the surrounding phase:

$$\gamma_{sl\,drop} = \sigma_s + \sigma_{l\,drop} - 2\sqrt{\sigma_s^D \cdot \sigma_{l_{drop}}^D} - W_{sl_{drop}}^P$$ Equation 47

$$\gamma_{sl\,bulk} = \sigma_s + \sigma_{l\,bulk} - 2\sqrt{\sigma_s^D \cdot \sigma_{l_{bulk}}^D} - W_{sl_{bulk}}^P$$ Equation 48

W_{sl}^{P} is the polar fraction of the work of adhesion, i.e. the interactions between the particular liquid and the solid.

If equations 46, 47 and 48 are combined then the following relationship is obtained:

$$\sigma_{l_{drop}} - \sigma_{l_{bulk}} + \gamma_{ll_{drop/bulk}} \cdot \cos\theta = 2\sqrt{\sigma_s^D} \cdot (\sqrt{\sigma_{l_{drop}}^D} - \sqrt{\sigma_{l_{bulk}}^D}) + W_{sl_{drop}}^P - W_{sl_{bulk}}^P \quad \text{Eq. 49}$$

11.2.7.2 SCHULTZ 1

In the "SCHULTZ 1" method only a single drop liquid is used and the surrounding phase is changed instead. The drop liquid used is normally water; the bulk phase is a liquid which is immiscible with water and with a lower density than water.

As in the FOWKES method the calculation of the **polar** and **disperse** fractions of the surface energy is carried out in **two steps**.

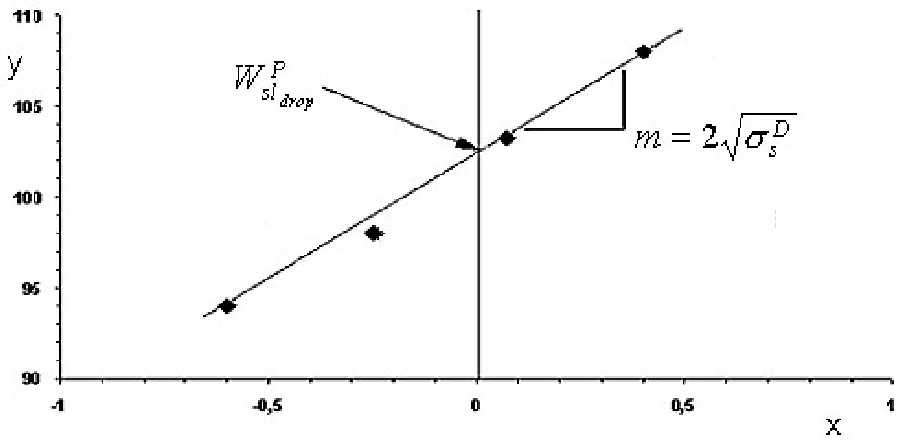
At first the contact angle of water on the solid is measured in a range of purely disperse interacting liquids. Owing to the nonpolar character of the surrounding phase the term $W_{sl_{bulk}}^{P}$ can be deleted from equation49. Equation 49 can then be adapted to conform with the general equation for a straight line:

$$y = mx + b \quad \text{Equation 50}$$

to give:

$$\underbrace{\sigma_{l_{drop}} - \sigma_{l_{bulk}} + \gamma_{ll_{drop/bulk}} \cdot \cos\theta}_{y} = 2\underbrace{\sqrt{\sigma_s^D}}_{m} \cdot \underbrace{(\sqrt{\sigma_{l_{drop}}^D} - \sqrt{\sigma_{l_{bulk}}^D})}_{x} + \underbrace{W_{sl_{drop}}^P}_{b} \quad \text{Eq. 51}$$

If the term y is plotted against x then the disperse fraction of the surface energy of the solid σ_s^D is can be calculated directly from the slope and $W^P_{sl_{drop}}$ from the y-axis intercept.



In the **second step** the **polar fraction** of the surface energy of the solid is determined by using several surrounding phases which have polar fractions. As the term $W^P_{sl_{drop}}$ from equation 49 is now known, the polar fraction of the adhesion energy between the solid and the surrounding phase $W^P_{sl_{bulk}}$ can be calculated for each individual surrounding phase.

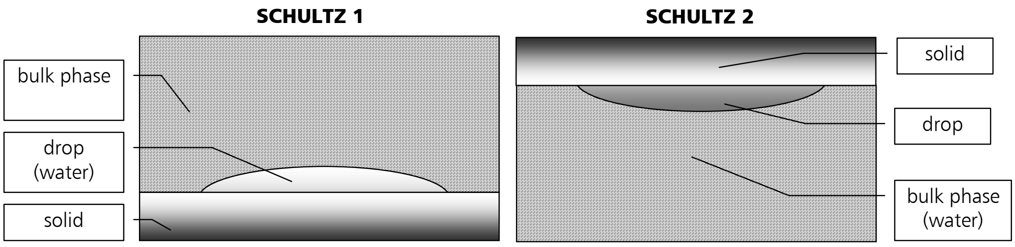
According to FOWKES, this adhesion energy can be calculated from the geometric mean between the polar fractions of the surface tensions of the participating phases:

$$W^P_{sl_{bulk}} = 2 \cdot \sqrt{\sigma_s^P} \cdot \sqrt{\sigma^P_{l_{bulk}}} \qquad \text{Equation 52}$$

As a result, if $W^P_{sl_{bulk}}$ is plotted against $\sigma^P_{l_{bulk}}$ then the required term σ_s^P can be obtained from the slope of the regression curve.

11.2.7.3 SCHULTZ 2

In the SCHULTZ 2 method it is not the heavier liquid which is used as the drop liquid but the lighter one; the heavier liquid forms the surrounding phase. In order for this to be possible the test arrangement must be inverted: the drop is not present as a sessile drop on the solid but is suspended from it as a pendant drop:



In this arrangement the surrounding phase is retained and the contact angles of various drop liquids are measured. The advantage when compared with the SCHULTZ 1 method is that the contact angles of the drop phase to be measured are larger and can therefore be measured more accurately.

As in SCHULTZ 1 the disperse fraction of the surface energy of the solid σ_s^D is measured first by using purely disperse interacting liquids. The difference from the calculation for SCHULTZ 1 is that the term $W_{sl_{bulk}}^P$ is obtained from the intercept of the regression curve with the y-axis on the plot, whereas the term $W_{sl_{drop}}^P$ is deleted from equation 49.

In the second step the term $W_{sl_{drop}}^P$ in equation 49 is calculated from the contact angles of drop liquids with polar fractions for each test liquid. The polar of the surface energy of the solid σ_s^P is obtained in a similar way to SCHULTZ 1 by using the equation

$$W_{sl_{drop}}^P = 2 \cdot \sqrt{\sigma_s^P} \cdot \sqrt{\sigma_{l_{drop}}^P}$$ Equation 53.

11.2.8 The acid-base method according to OSS & GOOD

OSS and GOOD also differentiate between a polar and a disperse fraction of the surface energy. However, in contrast to the previously described authors, they describe the polar fraction with the help of the **acid-base model according to Lewis**. According to this model, the polar fraction of the surface energy of the solid and the surrounding drop liquid is split into an electron acceptor fraction corresponding to a Lewis acid (="electron receiving" fraction) $\sigma^+$and an electron donor corresponding to a Lewis base (="electron donor" fraction) σ^-. Owing to the attraction of opposite charges there are interactions between the particular counter poles of the polar components of the solid and the liquid. The Equation for the surface tension of FOWKES and OWENS, WENDT, RABEL, KAELBLE (Equation 37) is adapted accordingly:

$$\gamma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^+ \cdot \sigma_l^-} + \sqrt{\sigma_s^- \cdot \sigma_l^+}) \qquad \text{Eq. 54.}$$

In order to calculate the 3 fractions of the surface energy of a solid from contact angle data equation 54 is combined with YOUNG's Equation:

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \qquad \text{Equation 55}$$

to obtain

$$(1 + \cos\theta)\sigma_l = 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^+ \cdot \sigma_l^-} + \sqrt{\sigma_s^- \cdot \sigma_l^+}) \qquad \text{Eq.56}$$

In order to solve this equation, i.e. to determine the disperse fraction σ_s^D, the acid fraction σ_s^+ and the base fraction σ_s^- of the solid, contact angle data from at least 3 test liquids are required; at least 2 of these must have a known acid and base fraction >0.

Moreover, at least one of the liquids must have equal basic and polar parts. Usually water is chosen for this purpose because it serves as neutral point in the LEWIS scale.

11.2.9 Predicting the wetting behavior: the "wetting envelope"

The "wetting envelope" is not an independent calculation method for the polar and disperse fractions of the surface energy of a solid, but only a special type of presentation. It can be used for all surface energy calculation methods which provide a polar fraction and a disperse fraction in the result.

With the help of the wetting envelope and a knowledge of the polar and disperse fractions of the surface energy of a solid it is possible to **predict whether a particular liquid**, whose surface tension components are also known, will **wet** the solid completely. The following relationships make this possible:

A liquid will wet a solid surface completely when the work of adhesion W_{sl} between the solid surface and the liquid is greater than work of cohesion W_{ll} within the liquid. The difference between these two quantities is known as the spreading pressure $S_{l/s}$:

$$S_{l/s} = W_{sl} - W_{ll}$$ Equation 57;

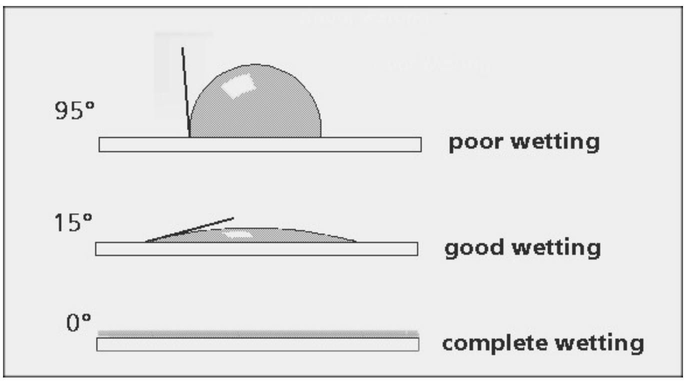
this means that a liquid will wet a solid when the spreading pressure is positive.

The work of adhesion can also be described with the help of the contact angle between the liquid and the solid and surface tension of the liquid:

$$W_{sl} = \sigma_l(\cos\theta + 1)$$ Equation 58

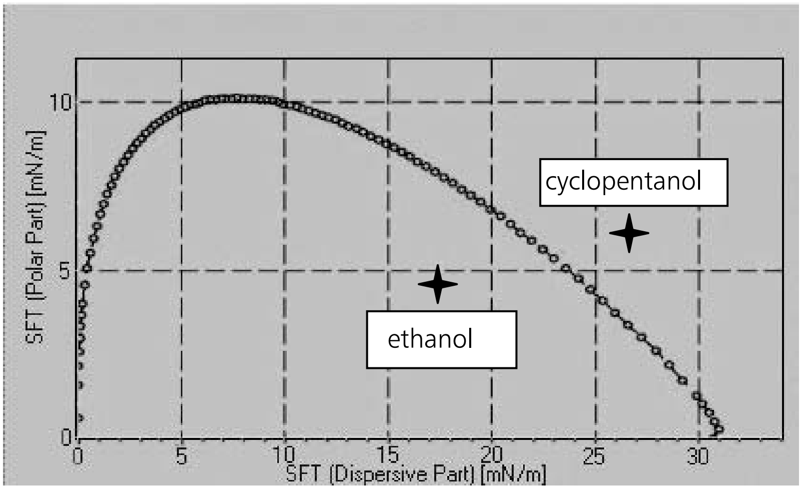
As according to DUPRÉ W_{ll} is defined as $2 \cdot \sigma_l$; this means that for a contact angle of 0° ($\cos\theta = 1$) the spreading pressure $S_{l/s}$ is 0 and the liquid will wet the solid completely.

The following figure shows the connection between contact angle and wettability:



In order to represent the wetting envelope the methods described for the determination of the disperse and polar fractions of the surface energy (FOWKES; OWENS, WENDT, RABEL and KAELBLE; WU) are reversed: disperse and polar fractions of the solid are known (from a measurement or from the literature); the corresponding equations are used instead to calculate the polar and disperse fractions of the liquid which have a value of $\cos\theta = 1$ for the solid under investigation. By plotting the polar fraction against the disperse fraction a curve is produced for $\cos\theta = 1$ which starts at the origin (0/0), attains a maximum value and then returns to the X-axis. The area enclosed within this curve is the wetting envelope or wetting range; all liquids whose data lie within this enclosed area will wet the corresponding solid.

The procedure is demonstrated below using two liquids as an example:



The following Table shows the data used for the above figure, this was taken from the DSA3 liquid database. The values for ethanol lie within the wetting envelope; this means that we can expect that ethanol will wet the solid. In contrast, cyclopentanol lies outside the envelope and should therefore not wet the solid.

Liquid	**Disperse fraction**	**Polar fraction**	**Wetting behavior**
Ethanol	17.5	4.6	wetted completely
Cyclopentanol	27.2	5.5	not wetted completely

11.3 Measuring the contact angle

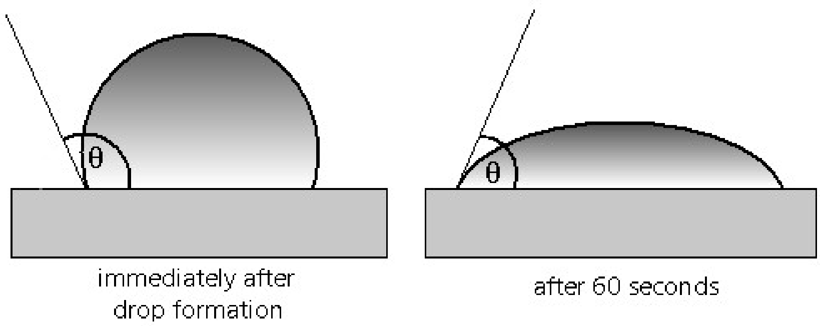
The previous section explained the various methods of calculating the surface energy from contact angle data. In this section the theory of contact angle measurement is explained. All calculation methods (except for SCHULTZ 2) are based on the sessile drop method, i.e. drops of liquid are deposited on a solid surface (as smooth and horizontal as possible).

A differentiation is made between the various ways of measuring the drop:

- A contact angle can be measured on **static drops**. The drop is produced before the measurement and has a constant volume during the measurement.
- A contact angle can be measured on **dynamic drops**. The contact angle is measured while the drop is being enlarged or reduced; the boundary surface is being constantly newly formed during the measurement. Contact angles measured on increasing drops are known as "**advancing angles**"; those measured on reducing drops as "**retreating angles**".

11.3.1 Static contact angles

In a static contact angle measurement the size of the drop does not alter during the measurement. However, this does not mean that the contact angle always remains constant; on the contrary, interactions at the boundary surface can cause the contact angle to change considerably with time. Depending on the type of time effect the contact angle can increase or decrease with time.



For example, these interactions could be:

- Evaporation of the liquid
- Migration of surfactants from the solid surface to the liquid surface
- Substances dissolved in the drop migrating to the surface (or in the opposite direction),
- Chemical reactions between the solid and liquid,
- The solid being dissolved or swollen by the liquid.

It may be a good idea to choose to measure the static contact angle when its variation as a function of time is to be studied. A further advantage of static contact angle measurement is that the needle does not remain in the drop during the measurement. This prevents the drop from being distorted (particularly important for small drops). In addition, when determining the contact angle from the image of the drop it is possible to use methods which evaluate the whole drop shape and not just the contact area.

Certain materials which don't show a fully rigid surface (e.g. rubber) are better being tested with static measurements. In such cases, dynamic contact angles are poorly reproducable.

However, changes with time often interfere with the measurement. There is also a further source of error: as the static contact angle is always measured at the same spot on the sample any local irregularities (dirt, inhomogeneous surface) will have a negative effect on the accuracy of the measurement. This error can be averaged out in dynamic contact angle measurements.

11.3.2 Dynamic contact angle

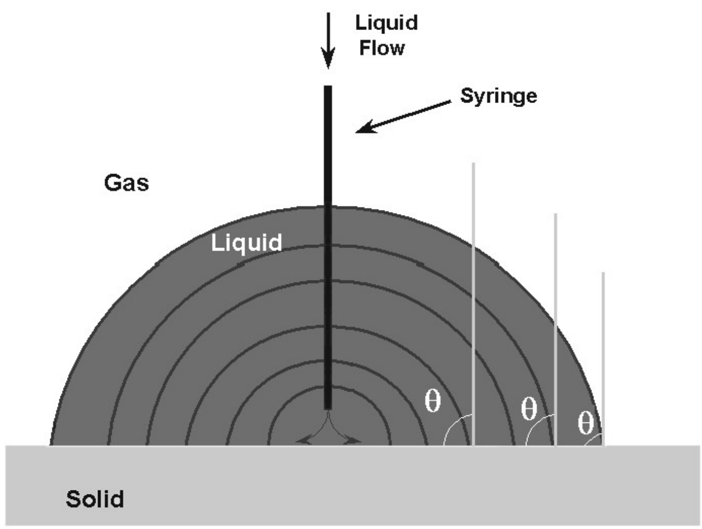
Dynamic contact angles describe the processes at the liquid/solid boundary during the increase in volume (advancing angle) or decrease in volume (retreating angle) of the drop, i.e. during the wetting and dewetting processes.

A boundary is not formed instantaneously but requires some time before a dynamic equilibrium is established. This is why a flow rate which is too high should not be selected for measuring advancing and retreating angles, as otherwise the contact angle will be measured at a boundary which has not been completely formed. However, it should also not be too slow as the time effects mentioned above will then again play a role. In practice flow rates between 5 and 15 µl/min can be recommended; higher flow rates should only be used for the simulation of dynamic processes.

For high-viscosity liquids (e.g. glycerol) the rate will tend to approach the lower limit.

11.3.2.1 Advancing angle

During the measurement of the advancing angle the syringe needle remains in the drop throughout the whole measurement. In practice a drop with a diameter of about 3-5 µl (with the needle of 0.5 mm diameter which is used in KRÜSS measurement systems) is formed on the solid surface and then slowly increased in volume. At the beginning, the contact angle measured is not independent from the drop size because of the adhesion to the needle. At a certain drop size the contact angle stays constant; in this area the advancing angle can be measured properly.

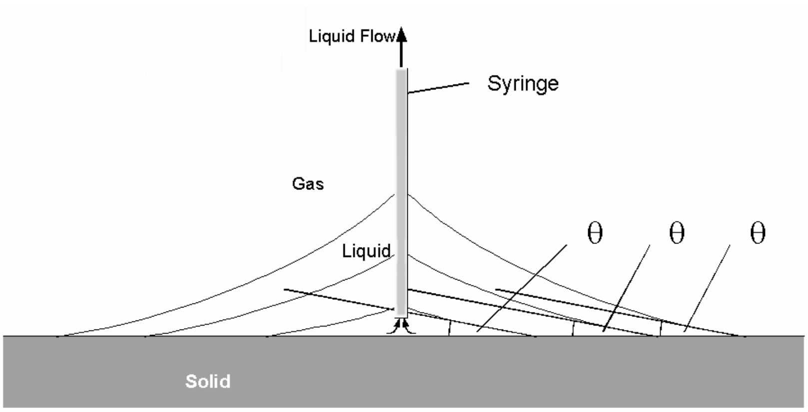


As a result of the wetting process, advancing angles always simulate a fresh surface for the contact angle; this is formed immediately after the creation of the contact between the liquid and the surface. This type of measurement is therefore the most reproducible way of measuring contact angles. As a result, advancing angles are normally measured in order to determine the surface free energy of a solid.

11.3.2.2 Receding angle

During the measurement of the receding angle the contact angle is measured as the size of the drop is being reduced, i.e. as the surface is being de-wetted. By using the difference between the advancing and the receding angles it is possible to make statements about the roughness of the solid or chemical inhomogeneties; however, the receding angle is not suitable for calculating surface energies.

In practice a relatively large drop with a diameter of approx. 6 mm is deposited on the solid and then slowly reduced in size with a constant flow rate.



The same guiding limits and conditions apply here as for the measurement of the advancing angle (see Section 11.3.2.1).

11.3.3 Methods of evaluating the drop shape

The basis for the determination of the contact angle is the image of the drop on the drop surface. In the DSA1 program the actual drop shape and the contact line (baseline) with the solid are first determined by the analysis of the grey level values of the image pixels. To describe this more accurate, the software calculates the root of the secondary derivative of the brightness levels to receive the point of greatest changes of brightness. The found drop shape is adapted to fit a mathematical model which is then used to calculate the contact angle. The various methods of calculating the contact angle therefore differ in the mathematical model used for analyzing the drop shape. Either the complete drop shape, part of the drop shape or only the area of phase contact are evaluated. All methods calculate the contact angle as $\tan\theta$ at the intersection of the drop contour line with the solid surface line (base line).

In the following sections the different drop shape analysis methods are briefly described.

11.3.3.1 Ellipse method (Tangent-1)

The complete profile of a sessile drop is adapted to fit a general conic section equation. The derivative of this equation at the intersection point of the contour line with the baseline gives the slope at the 3-phase contact point and therefore the contact angle. If dynamic contact angles are to be measured, this method should only be use when the drop shape is not distorted too much me the needle.

11.3.3.2 Polynomial method (Tangent 2)

That part of the profile of a sessile drop which lies near the baseline is adapted to fit a polynomial function of the type ($y=a+bx+cx^{0,5}+d/\ln x+e/x^2$). The slope at the 3-phase contact point at the baseline and from it the contact angle are determined using the iteratively adapted parameters.

This function is the result of numerous theoretical simulations. The method is mathematically accurate, but is sensitive to distortions in the phase contact area caused by contaminants or surface irregularities at the sample surface.

As only the contact area is evaluated, this method is also suitable for dynamic contact angles. Nevertheless, this method requires an excellent image quality, especially in the region of the phase contact point.

11.3.3.3 Circle fitting method

In this method the drop contour is fitted to a segment of a circle. The contact angle is not calculated by fitting a circular segment function to the contour. As the method uses the whole drop contour, the needle should not remain in the drop. The method is only suitable for static measurements.

11.3.3.4 Height-Width method)

As for the circle fitting method, the drop shape is considered a circular segment. The height and width of the rectangle which encloses this circular segment is determined. This method is less robust than the circle fitting as only the two three-phase contact points and the vertex are used for the analysis and not the whole drop contour.

11.3.3.5 Young-Laplace (sessile drop fitting)

The YOUNG-LAPLACE fitting considers the theoretical shape of a drop under gravity. After fitting the YOUNG-LAPLACE Equation the contact angle is determined as the slope of the contour line at the three-phase contact point. This method uses the whole contour of the drop.

This model assumes a symmetric drop shape; therefore it cannot be used for dynamic contact angles where the needle remains in the drop.

If the magnification scale of the drop image is known (determined by using the syringe needle in the image) then the interfacial tension can also be determined; however, the calculation is only reliable for contact angles above 30°.

The physical-mathematical principles of the YOUNG-LAPLACE method are described in more detail in ch. 11.4.1, which is concerned with the calculation of the surface tension of pendant drops.

11.4 Measuring the surface tension of pendant drops

If a drop of liquid is hanging from a syringe needle then it will assume a characteristic shape and size from which the surface tension can be determined.

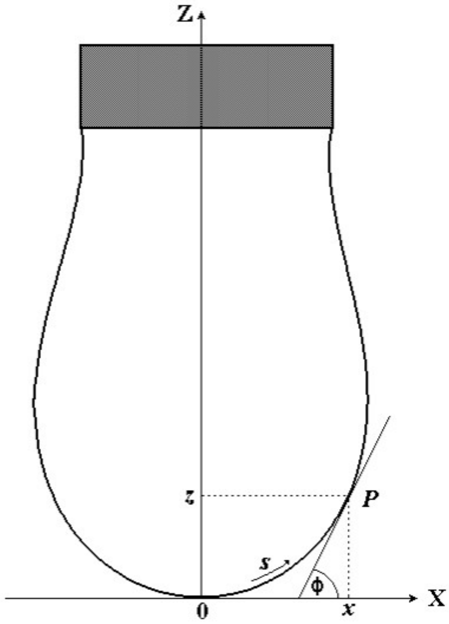
The force of gravity acting on the drop and depending on the particular height corresponds to the LAPLACE pressure, which is given by the curvature of the drop contour at this point. The LAPLACE pressure results from the radii of curvature standing vertically upon one another in the following way:

$$\Delta p = \sigma \cdot \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$ Equation 59

This equation describes the difference between the pressure below and above a curved section of the surface of a drop with the principal radii of curvature r_1 and r_2. The pressure difference Δp is the difference in pressure between the outside of the drop and its inside.

11.4.1 The basic drop contour equation

For a pendant drop which is rotationally symmetrical in the z-direction then, based on equation 59, it is possible to give an analytically accurate geometric description of the principal radii of curvature. The tangent at the intersection of the z-axis with the apex of the drop forms the x-axis. The drop profile is given by pairs of values (x,z) in the x-z-plane.



In hydromechanical equilibrium the following relationship applies

$$\Delta p_{apex} - \Delta p_P = z \cdot \Delta\rho \cdot g$$ Equation 60

(Δp_{apex} = pressure difference at apex; Δp_P = pressure difference at Point P (x,z); $\Delta\rho$ = difference in density between the drop liquid and its surroundings; g = acceleration due to gravity)

With the principal curvatures k (reciprocal value of principal curvature radius r) and the YOUNG-LAPLACE Equation (Equation 59) we obtain:

$$\Delta p_{apex} = \sigma \cdot \left(k_{apex,1} + k_{apex,2}\right)$$ Equation 61

$$\Delta p_p = \sigma \cdot \left(k_{p,1} + k_{p,2}\right)$$ Equation 62

$k_{apex,1(2)}$ = principal curvatures at apex

$k_{P,1(2)}$ = principal curvatures at Point P (x,z)

Because of the axial symmetry of the drop, the principal curvatures at the apex are the same in all directions (→ k_{apex}). From differential geometry the analytical expressions for the curvatures of the principal normal sections at Point P (x,z) are known:

$$k_{p,1} = \frac{d\Phi}{ds} = \left(\frac{d^2z}{dx^2}\right)\cdot\left(1+\left(\frac{dz}{dx}\right)^2\right)^{-3/2}$$ Equation 63

$$k_{p,2} = \frac{\sin\Phi}{x} = \left(\frac{dz}{dx}\right)\cdot\frac{1}{x}\cdot\left(1+\left(\frac{dz}{dx}\right)^2\right)^{-1/2}$$ Equation 64

From equations 60 to 64 we obtain:

$$\frac{d\Phi}{ds} = 2k_{apex} - \frac{z\cdot\Delta\rho\cdot g}{\sigma} - \frac{\sin\Phi}{x}$$ Equation 65

(s= length of arc along the drop profile, Φ = angle between the tangents at Point P (x,z) and the x-axis.

Equation 65 describes the profile of a pendant drop in hydromechanical equilibrium. The Equation is converted into a dimensionless form to solve it. The following definitions are used:

$$X = \frac{x}{a};\ Z = \frac{z}{a};\ S = \frac{s}{a};\ B = \frac{1}{a\cdot k_{apex}};\ \text{with: } a = \sqrt{\frac{\sigma}{\Delta\rho\cdot g}}$$

B = dimensionless form parameter of the pendant drop

a = capillary constant

With these definitions Equation 65 can also be expressed in the following way:

$$\frac{d\Phi}{dS} = \frac{2}{B} - Z - \frac{\sin\Phi}{X};\ \frac{dX}{dS} = \cos\Phi;\ \frac{dZ}{dS} = \sin\Phi$$ Equation 66

At the apex the limiting conditions X = Z = S = Φ = 0 apply. This results in:

$$\frac{\sin\Phi}{X} = \frac{1}{B}$$ Equation 67

B is the only parameter to describe the shape of the drop profile. It is known as the **shape parameter**. In addition, it can be seen that the surface tension σ can be calculated for a known difference in density Δρ if the relative size ratio a of a measured drop can be determined for the corresponding theoretical drop profile.

Equation 67 is, together with the limiting conditions from Equation 66, known as the **fundamental equation for a pendant drop**.

By varying the form parameter B it is possible to calculate theoretical drop profiles after carrying out a numerical integration method. If the theoretical drop profile corresponds to the measured drop profile then the surface tension can be calculated. The problem in measuring the interfacial tension therefore consists in determining the correct theoretical drop profile for the measured drop exactly and rapidly.

11.4.2 The robust shape comparison method

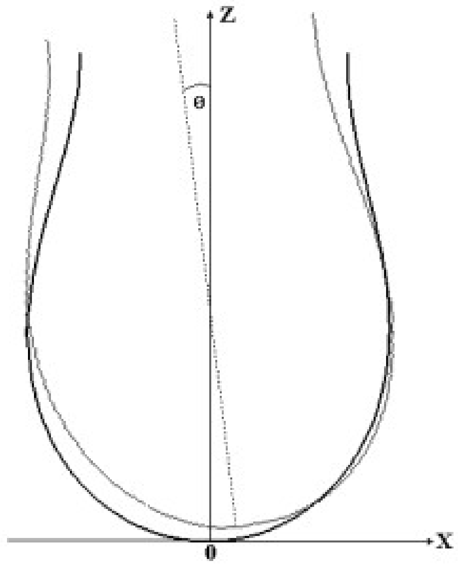
Various groups of methods exist for solving the problem mentioned above. In the DSA1 program the robust shape comparison method is used. This method is a statistical method which is characterized by its stability against "outliers". In this way even low-quality drop images can still be evaluated.

A series of drop profile co-ordinates is used for the evaluation. The measured profile is compared with the theoretical profile. The comparison is not made directly via the profile points, but via their vectors. An advantage of this method is that it is possible to optimize the individual parameters used independently.

For a more accurate observation of the mathematical details of the individual optimization steps and correction methods please refer to the technical publications. The error function E used in the optimization is a function of the form parameter B, the capillary constant a (which includes the surface tension), the position of the apex (x_0, z_0) (co-ordinate origin) and the angular variation Θ of the drop from the plane of symmetry.

$$E = E(B, a, (x_0, z_0), \Theta)$$ Equation 68

The angular variation Θ of the drop from the plane of symmetry describes the variation of the vertical drop axis from the normal axis (z-axis). For small variations (± 0.1°) the correction does not cause any problems.



In the evaluation of the image a further quantity appears which also needs to be taken into consideration: the height-width ratio AR (**A**spect **R**atio) of the image pixels in the drop image. By adaptation of the described parameters B, θ and AR the error function E_{rsc} (**r**obust **s**hape **c**omparison) from equation 68 can be minimized by the robust shape comparison:

$$E_{rsc} = E\left(B, \left(x_0(\Theta), z_0(\Theta)\right), AR\right)$$ Equation 69