Sigma 700/701

User Manual - OneAttension

Original instructions

Force Tensiometer

MANUAL23832-5

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1 Introduction

The Sigma tensiometer system is a modular high performance surface tension/contact angle meter. It expands from a basic all round Tensiometer into a highly sophisticated precision measuring system for R&D applications. The Sigma 700/701 tensiometer is a computer-controlled instrument for the measurement of:

- Surface and Interfacial tension (ST & IT)
- Single Force Curve measurements with the Du Noüy ring method
- Continuous Surface and Interfacial tension measurements with the Wilhelmy plate method
- Critical Micelle Concentration (CMC)
- Dynamic Contact Angles (DCA)
- Powder and Porous Solid Wettability
- Single Fiber Wettability
- Adsorption Behavior of Solids
- Surface Free Energy of Solids
- Density of liquids and solids
- Adhesion force
- Sedimentation kinetics

The instrument has a modular design, which allows addition of a variety of devices. In addition to the basic Sigma Measuring Unit it can be equipped with:

- Magnetic stirrer
- Temperature measuring
- pH measuring
- 1 or 2 Dispensers for CMC measurements
- Water Bath
- Thermostatic water jacket for sample liquid temperature control (-20 °C – 200°C)
- Sample holders of different design

The open design and modular construction allow you to adapt your instrument to a wide variety of applications.

The software will allow you to easily perform a variety of pre-programmed experiments. The data is stored to your hard drive and can be retrieved and analysed later. If you wish to utilize other data reduction software the data files are easily exported.

Inside this manual you will find information on how to use your Sigma tensiometer. You will also find brief reviews of the concepts involved in your measurements and some practical advice on the techniques involved. In order to obtain the maximum performance from your instrument you should read this manual and keep it available for reference.

2 Safety

WARNING!
The safety requirements listed in this manual must be followed in order to avoid personal injury and damage to the instrument. If the equipment is used in a manner not listed in this manual, protection provided by the equipment may be impaired.

WARNING!
RISK OF ELECTRICAL SHOCK. Do not connect this instrument to electrical power if the enclosure is damaged or any of the covers or panels are removed. Make sure the voltage rating on the instrument matches the line voltage available. Make sure the power cord is not damaged and it is properly connected to the instrument and a power outlet with protective earthing. Make sure that the power cord is easily accessible after the equipment has been installed and set at its working position.

WARNING!
RISK OF ELECTRICAL SHOCK OR FIRE HAZARD. The instrument has been designed for indoor use only. Do not expose it to rain, snow or dust. During storage or transport the instrument should be kept dry. Temperatures below 0°C and above 70°C should be avoided. Do not operate at ambient temperatures below 15°C and above 30°C.

When handling flammable liquids, use a minimum sample volume that is required for successful measurement.

Ensure prevention of Electrostatic Discharge (ESD) when handling flammable liquids. Contact your local authorities for information on ESD prevention practices.

Do not heat flammable sample liquids to temperatures higher than T–25 °C where T is fire point of the sample liquid.

WARNING!
RISK OF INJURY. Do not configure the instrument with parts that are not supplied by Biolin Scientific and not intended to be used with Attension instruments. Do not install substitute parts that are not described in this manual. Do not perform any modifications to the product.

If dangerous liquids are used, adequate protection such as proper ventilation, safety glasses, etc., should be used: refer to the safety information from the supplier and general safety regulations in your country. Carry out appropriate decontamination if equipment is exposed to hazardous material.

WARNING!
RISK OF BURNS. Exercise caution when touching heated sample vessels (optional). The vessel surface will reach dangerous temperatures when heated. The vessels are marked with hot surface warning symbol.

Platinum Wilhelmy plate/rod is an excellent catalyst for oxidation of methanol vapor. This reaction is very exothermic. In experiments in which the Wilhelmy plate/rod is positioned above reagent-grade methanol this reaction may cause dangerous heating of the plate/rod. Be aware of this phenomenon and take appropriate precautions.

CAUTION!

Make sure that the power is switched off when making any electrical connections (apart from the USB cables). Connecting cables with power on may damage instrument electronics. To disconnect the instrument, after turning the instrument off, remove the power cord plug from the electric outlet.

3 Physical Description

This section describes the physical construction of your Sigma tensiometer. All necessary hardware, software and accessories are included in the basic Sigma instrument making it possible to take the instrument into use directly from its shipping crate.

3.1 Measurement Unit

The basic measurement unit consists of the following parts:

- Auto-locking and auto-calibrating extended range microbalance (Sigma 700) or manually locked and calibrated super sensitive torsion wire electrobalance (Sigma 701)
- Lifting stage with long movement range for large samples
- Main body containing electronics, power supply and communication interface
- Membrane keyboard for manual operation of the stage, light and stirrer.
- Measuring chamber with wide opening and removable doors i.e. large working space
- Led lights for illumination of the measuring chamber
- Connectors for temperature probe, pH sensor and magnetic stirrer

3.2 Balance

The balance for your Sigma 700 or 701 tensiometer is in the upper housing of the measuring unit. The balance is suitable for all kind of surface/interfacial tension, CMC, dynamic contact angle, adsorption of solids, wettability of powders and density measurements. Hook comes down from the balance and is used for hanging the probe used for the measurement. In Sigma 701 there is a travel lock that is located on top of the balance housing and looks like a small screw. Use this to lock the balance when the measuring unit is moved (even from table to table).

The stage of your Sigma tensiometer is lifted by a stepper motor. In order to ensure vibration-free movement the stage is attached to a glide with precision ball bearing balls steered by a precision rail of highest linearity. The speed of the stepper motor is detected by an optical encoder. There are safety switches, which stops the upward and downward movement of your stage automatically at the highest and lowest positions of the stage. The electronics and mechanic parts of the lifting system are protected from liquid spills by a rubber below.

3.3 Manual Membrane Keyboard

The built in Manual Membrane Keyboard shows the On-off status light and allows you to operate up-down movements of the sample stage, stirrer on-off and chamber light on-off outside the software control i.e. without PC control.

The ↑ and ↓ buttons control the relative distance between the probe and the vessel. If the ↑-button is continuously pressed the distance between the probe and the stage will decrease and the probe seems to be immersed into the vessel, and when the button is released the movement of the stage stops. Vice versa for the ↓-button.

The light button controls the chamber light On-Off status. Press once the light goes on and press another time the light turns off.

The whirl button controls the stirrer On-Off status. Press once the stirrer starts and press another time the stirrer stops. **Note! The stirrer is not included in the basic measurement unit.**

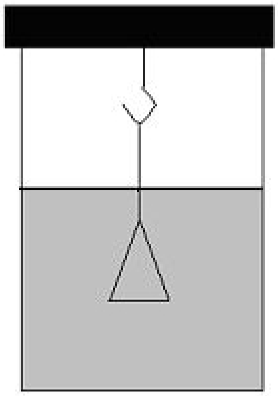
The yellow led informs if the power of the instrument is on (led is on) or not (led is dark).

3.4 Du Noüy Ring

Optional platinum/iridium ring is supplied in a protective transport case. The ring should be cleaned regularly after use and treated carefully to avoid deformation. Dimensions: R (ring) = 9.58 mm, r (wire)= 0.185mm.

A good way to store the ring is to immerse it in ethanol by first hanging it on a hook attached to a lid, which is then attached to a beaker filled half-full with ethanol. Then before using the ring again flush it with pure ethanol and water, or burn it with a Bunsen burner (ca. 1000 °C flame) for a short time (glowing yellow-red for a few seconds). In this way the ring will keep its form better and will not deform as easily as by putting it back to the wooden box after each measurement.

The ring that is used must have R/r ratios of around 52 or 26. This is because when the Du Noüy ring is used, a correction factor has to be applied. The software includes correction factor for rings with R/r of 52 or 26. You can read more about the correction in the Theory section of this manual.



3.5 Wilhelmy Plate

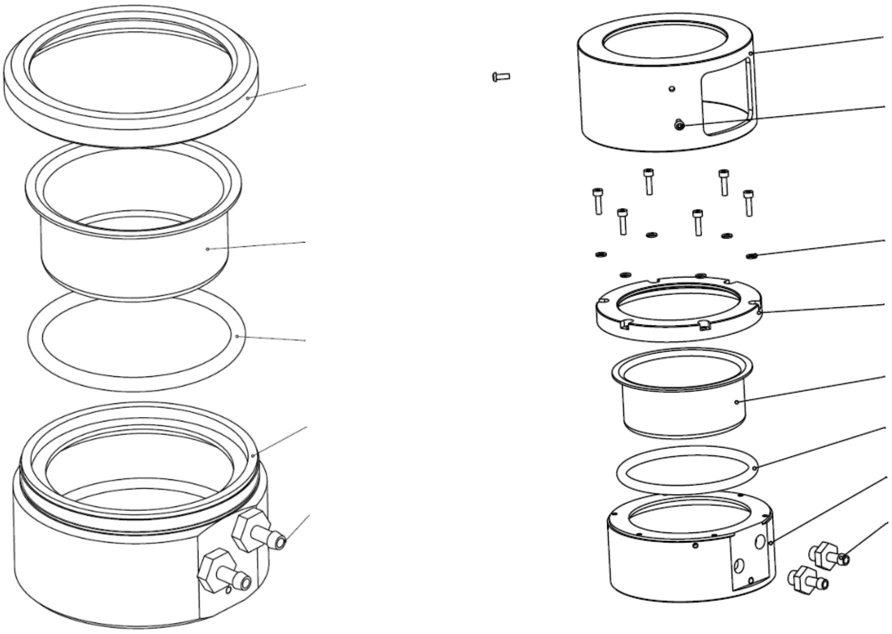
Optional platinum micro-roughened Wilhelmy plate is supplied in a plastic box. This should be cleaned regularly after use and treated carefully to avoid deformation. Dimensions: Width = 19.52 mm, Thickness = 0.1mm. The same cleaning procedure as for the Du Noüy ring applies for the Wilhelmy plate.

WARNING!
RISK OF BURNS. Platinum Wilhelmy plate/rod is an excellent catalyst for oxidation of methanol vapor. This reaction is very exothermic. In experiments in which the Wilhelmy plate/rod is positioned above reagent-grade methanol this reaction may cause dangerous heating of the plate/rod. Be aware of this phenomenon and take appropriate precautions.

3.6 Thermostatic vessel (optional)

Note! When using Thermostatic vessels and Magnetic stirrer, consider the intended operating temperatures. The Magnetic stirrer has a specified temperature range of -10 to 120 °C. Do not use the Thermostatic vessel at temperatures outside this range if Magnetic stirrer is attached. If temperatures outside this range are used, it is necessary to remove the stirrer.

As an option, T705 Thermostatic vessel from -10 to 100 °C or T705A Thermostatic vessel from -20 to 200 °C can be acquired. The T705 vessel is fixed with threads to make it liquid-tight. The vessel comes pre-assembled but in case you should notice a leakage of circulating fluid at some point, please reassemble the system with the flowing instructions.



T705 (left) and T705A (right) assemblies.

T705 vessel consists of four pieces: plastic vessel frame, O-ring, aluminium cup and plastic cover. The circulation fluids circulated between the plastic vessel frame and the aluminium cup, sealed by the O-ring and the cover. First insert the O-ring into the vessel. Make sure it’s properly set and in correct place. Next place the aluminium cup on top of it. Finally fix the sealing by fixing the cover part which is attached with threads. Use only moderate force by hand to tighten it to prevent damaging the threads.

In T705A vessel the aluminium cup and O-ring are mounted between the frame bottom and top with 6x screws and washers. Use only moderate force when tightening the screws. The PTFE cover is mounted with 2x screws. Hose couplings are mounted only after the cover has been mounted.

The thermostatic vessel is mounted on the sample stage by simply placing it on the sample stage so that the water quick connectors are pointing towards the back wall of the measuring chamber. The tubings from the thermostatic vessel are connected to quick release adapters on the back wall of the measuring chamber. **Note!** Position the tubings so that they are not in contact with measurement chamber doors.

The water circulator is connected to the other end of the adapters.

If the thermostatic vessel is purchased afterwards, then the adapters need to be installed first. This is done by attaching the adapters to the holes reserved for them using a lock nut.

3.7 Cleaning procedure

In all measurements done with Sigma 700/701, the cleanliness of the used probes and beakers is extremely important for reliable and reproducible results. The best cleaning procedure depends on the samples used. Here is a typical cleaning procedure when water or oil is used.

Cleaning of the glass beaker

Rinse **three times** with n-heptane (only after preceding tests with oil), afterwards with 2-propanol (also in case of unused beakers and after water testing). Rinse with hot tap water and afterwards thoroughly with deionized water/bi-distilled water. Please see water requirements below.

Laboratory dish washer with integrated deionized water with the required quality may be used if providing the required cleanliness. Be sure that all washing agents are removed completely before drying.

Cleaning of the platinum probe

Rinse **three times** with n-heptane; afterwards with deionized water and **heat it in the oxidizing flame** for approx. 5 s in an ethanol or natural gas burner to **red** heat.

Water used for the reference test

Bi-distilled or deionized water from a glass bottle with a surface tension of >70 mN/m at max. 25°C should be used. HPLC-grade water may be used if suitable.

Note: For pure water the following relationship between surface tension of water and temperature exists:

$$\frac{\Delta\sigma}{\Delta \mathrm{T}} = 0{,}15 \frac{mN}{m \times {}^{\circ}C}$$

σ = surface tension (mN/m)

T = temperature (K)

Cleaning the instrument

The exterior of the instrument can be cleaned with a damp cloth. Ensure that the surfaces are dried immediately after cleaning. If liquid is accidentally spilled on the instrument, wipe the instrument using a dry, clean cloth.

3.8 Maintenance

Only persons authorized by Biolin Scientific are allowed to perform maintenance and repairs on the instrument. In case repair is needed, contact Biolin Scientific or an authorized representative directly.

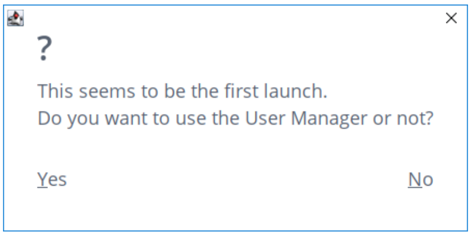
4 Software

The OneAttension software is supplied to you on a USB drive. The setup program will guide you through the installation. For detailed instructions, see OneAttension Sigma 700/701 Installation Manual.

4.1 Starting the OneAttension for the first time

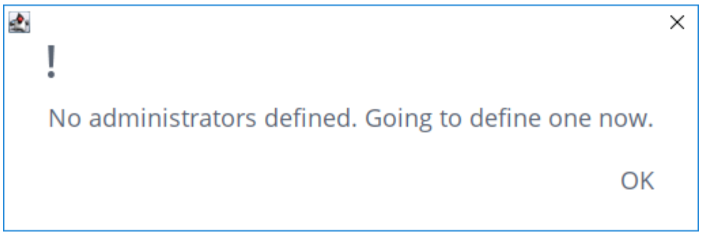
A Shortcut icon of OneAttension was created in installation. Turn on the instrument. Double-click icon to start software.

When starting the OneAttension program (located by default on the desktop and in the Start menu under Programs>OneAttension) for the first time, the software asks you whether you would like to use the User Manager option. The User Manager allows you to create each user their own accounts and set user levels. For more information, see paragraph 3.4.2. User manager.


?

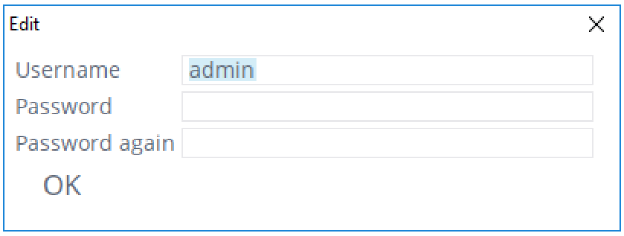
This seems to be the first launch.
Do you want to use the User Manager or not?

If User manager option is not selected, the software will open without the need of writing a password. If User manager option is selected, the software will ask you to define the Administrator first. Administrator is able to create new user accounts and manage the existing users.


!

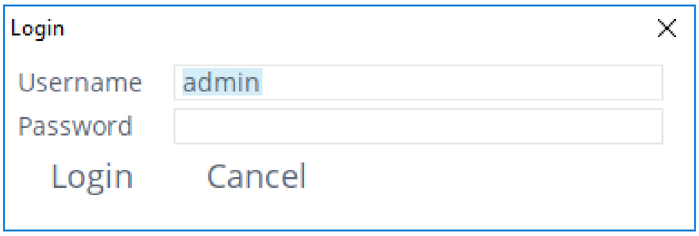
No administrators defined. Going to define one now.

Define the Username and password for the administrator.



Username: admin
Password:
Password again:

After creating the Administrator, you can login with the newly created account.

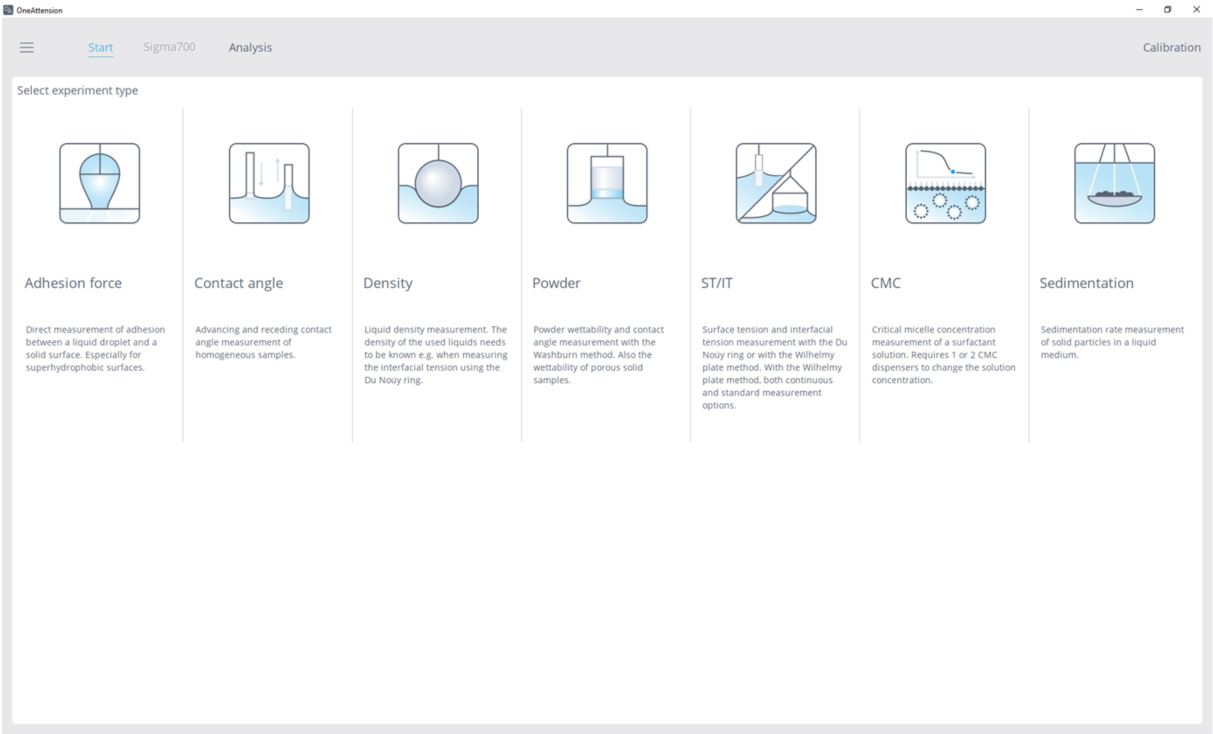


Username admin

Password

4.2 Start tab and Sigma700/701 tab

After login to the OneAttension software, with Sigma 700/701 is connected and turned on, the software will open on the **Start tab.** If you start OneAttension without Sigma 700/701 connected, **Start tab** will not be visible.



Select experiment type

Adhesion force

Direct measurement of adhesion between a liquid droplet and a solid surface. Especially for superhydrophobic surfaces.

Contact angle

Advancing and receding contact angle measurement of homogeneous samples.

Density

Liquid density measurement. The density of the used liquids needs to be known e.g. when measuring the interfacial tension using the Du Noüy ring.

Powder

Powder wettability and contact angle measurement with the Washburn method. Also the wettability of porous solid samples.

ST/IT

Surface tension and interfacial tension measurement with the Du Noüy ring or with the Wilhelmy plate method. With the Wilhelmy plate method, both continuous and standard measurement options.

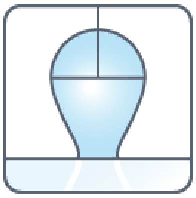
CMC

Critical micelle concentration measurement of a surfactant solution. Requires 1 or 2 CMC dispensers to change the solution concentration.

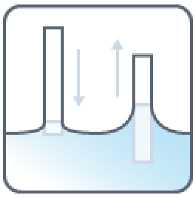
Sedimentation

Sedimentation rate measurement of solid particles in a liquid medium.

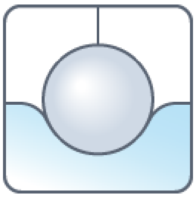
Your Sigma tensiometer is programmed to perform a series of experiments, which can be modified to suit your particular needs. The **Start tab** shows all experiment icons and by clicking an icon, a new measurement can be started. The experiment choices include Surface/Interfacial Tension with ring and plate, Contact Angle, Powder Wettability, Density, Adhesion force, Critical Micelle Concentration with ring and plate and Sedimentation kinetics. Top right corner of the **Start tab** also contains Calibration button which provides quick access to System diagnostics window (see 4.4 for more details).



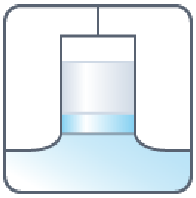
Adhesion force measurement



Contact angle experiment

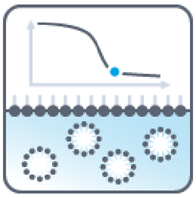


Density measurement



Powder wettability measurement

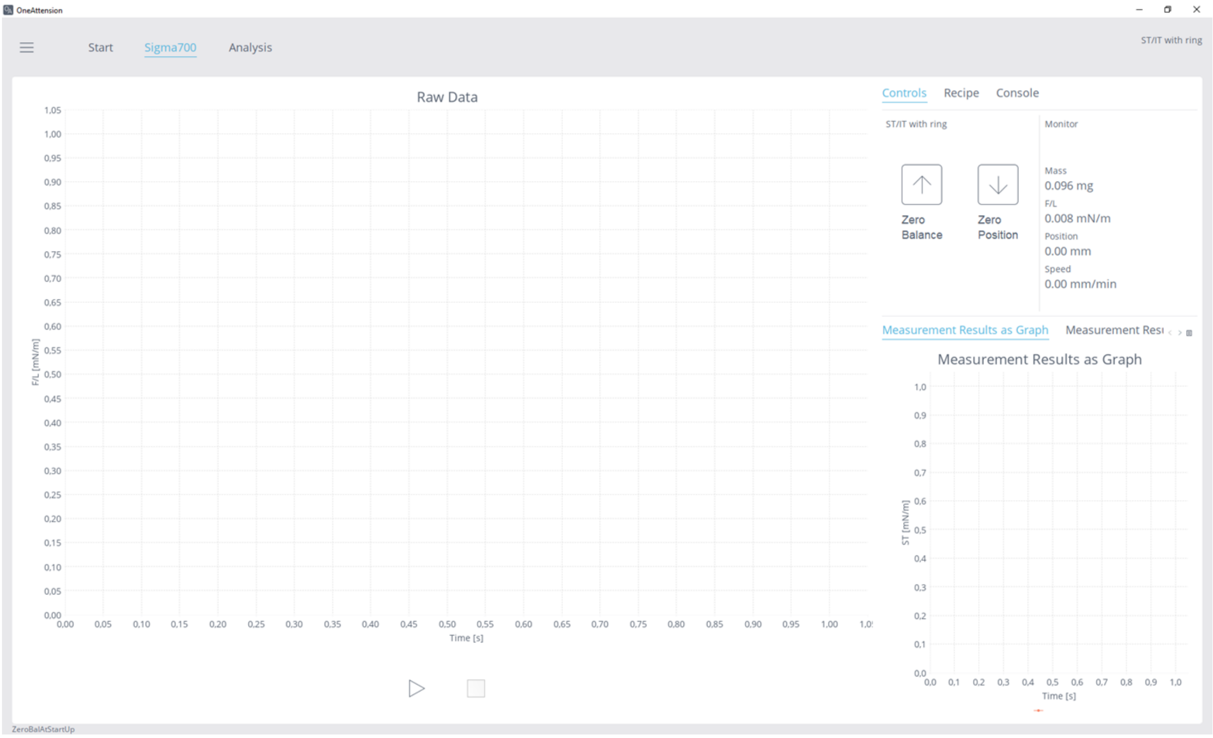
Surface tension/Interfacial tension measurement



Critical micelle concentration measurement

Sedimentation measurement

After selecting the experiment type, OneAttension will open **Sigma700 tab** or **Sigma701 tab** depending on your instrument.



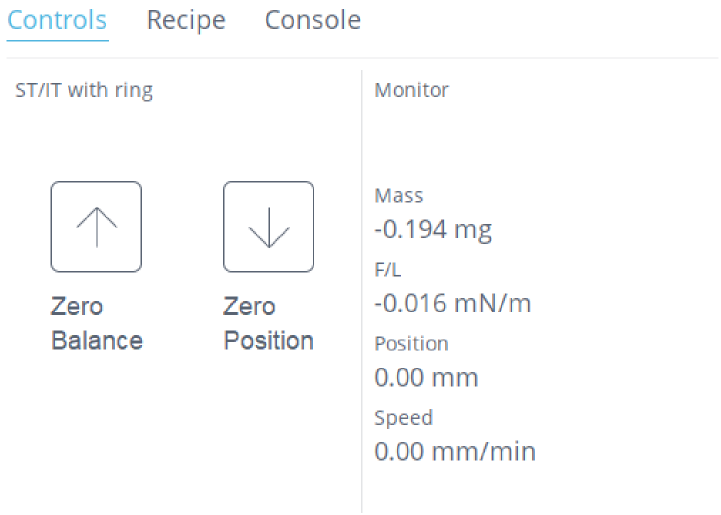
Mass
0.096 mg
F/L
0.008 mN/m
Position
0.00 mm
Speed
0.00 mm/min

On top right side of the **Sigma700 tab** there are Controls, Recipe and Console tabs available.

Experiments can be started and stopped at the buttons on bottom centre of the **Sigma700 tab**.

4.2.1 Controls tab

Controls tab contains control buttons for the instrument. Mass (mg), force (mN/m), the position (mm) and speed (mm/min) of the probe, temperature (°C) and pH (if temperature or pH probe is connected) are also shown in real time during the experiment on Controls tab.



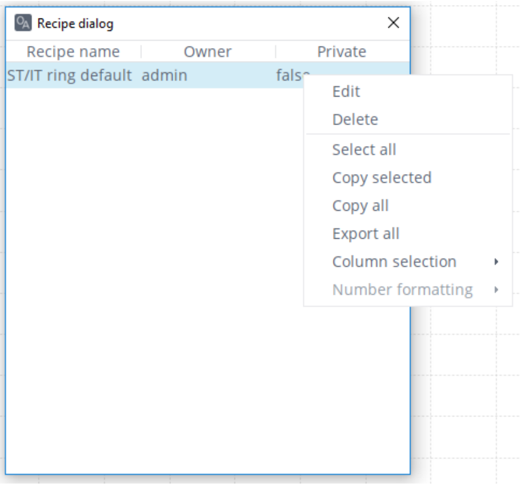
Mass
-0.194 mg
F/L
-0.016 mN/m
Position
0.00 mm
Speed
0.00 mm/min

◻	Stop: Stops all movement
↓	Moves probe down
↑	Moves probe up
Zero Balance	Zeroes the balance
Zero Position	Zeroes probe position

4.2.2 Recipe tab

Recipes contain a set of experiment parameters. Default recipe is loaded automatically when an experiment is selected. A recipe is considered default if its name contains the word "default" (case insensitive). If there's more than one candidate, the first one (or the first one owned by the current user) is selected. Users can create and save recipes, as well as browse and load them by clicking on the top right corner of Recipe tab. The measurement window will then automatically appear with the pre-defined values in the recipe.

Recipes can be edited or deleted from the recipe manager by right clicking on the recipe and proceeding from the pop-up menu. It is also possible to export all recipes in comma separated file (.csv/txt) or Excel (.xls/xlsx) or format.



Recipe name	Owner	Private
ST/IT ring default	admin	false

All the recipes have some common fields that are under Generic parameters, these include

Experiment name: The experiment has to have a name before the measurement can be started.

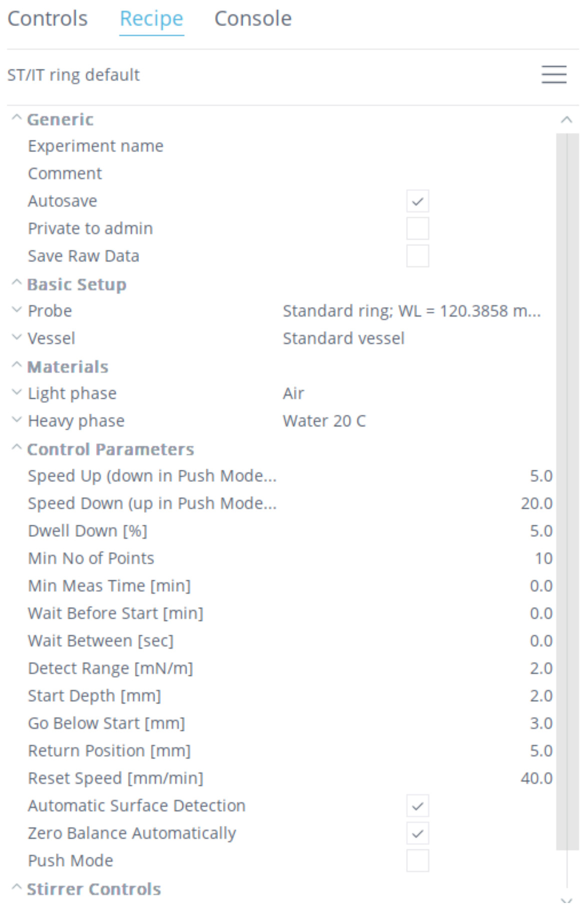
Comment: Some comment can be added.

Autosave: When autosave is chosen, the results are automatically saved. If not chosen the software will ask if you want to save the experiment when the experiment is closed.

Private to admin: Only the current user can see the results. If not chosen, results are available for all users. Option is only available if user manager is enabled.

Save raw data: If selected, the raw data is also saved (only for measurements where raw data and results differ from each other).

For detailed information about the other field in the recipe and how to conduct a measurement, please refer to the appropriate measurement chapter.



ST/IT ring default

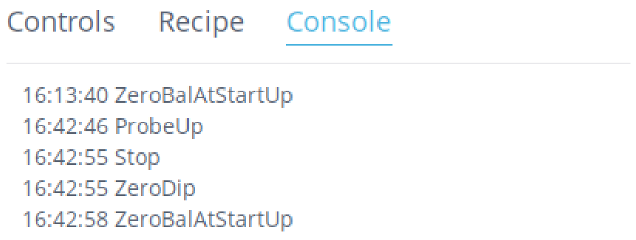
Generic	
Experiment name	
Comment	
Autosave	☑
Private to admin	☐
Save Raw Data	☐
Basic Setup	
Probe	Standard ring; WL = 120.3858 m…
Vessel	Standard vessel
Materials	
Light phase	Air
Heavy phase	Water 20 C
Control Parameters	
Speed Up (down in Push Mode…	5.0
Speed Down (up in Push Mode…	20.0
Dwell Down [%]	5.0
Min No of Points	10
Min Meas Time [min]	0.0
Wait Before Start [min]	0.0
Wait Between [sec]	0.0
Detect Range [mN/m]	2.0
Start Depth [mm]	2.0
Go Below Start [mm]	3.0
Return Position [mm]	5.0
Reset Speed [mm/min]	40.0
Automatic Surface Detection	☑
Zero Balance Automatically	☑
Push Mode	☐
Stirrer Controls	

You can also open a pre-defined experiment recipe by scanning a barcode that is saved to the barcode database (see 4.4.1). This can also be done when an experiment is opened. If a measurement is running, the software will ask you to abort it before opening the pre-defined experiment.

4.2.3 Console tab

Console tab records all the actions. This might be useful especially with long lasting automated measurements, when the user is not following the measurements in real-time.

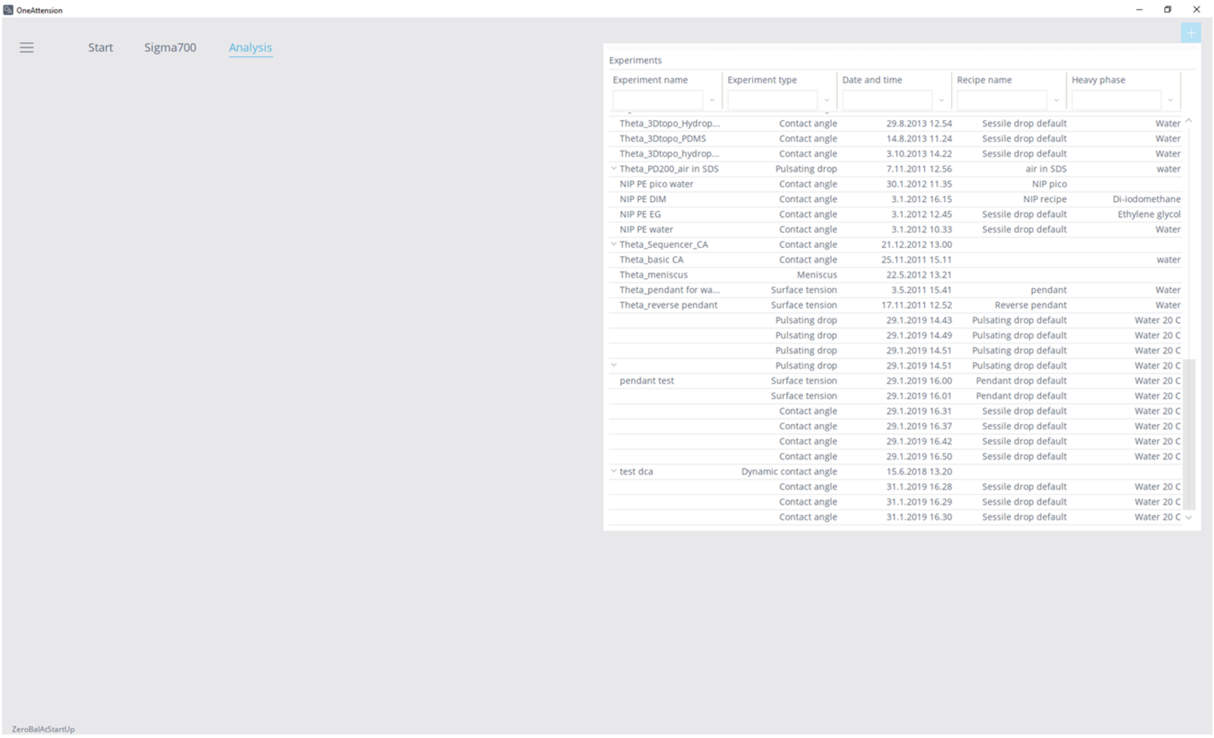
Console tab can be cleared by clicking "Clear all" below the console.



```
16:13:40 ZeroBalAtStartUp
16:42:46 ProbeUp
16:42:55 Stop
16:42:55 ZeroDip
16:42:58 ZeroBalAtStartUp
```

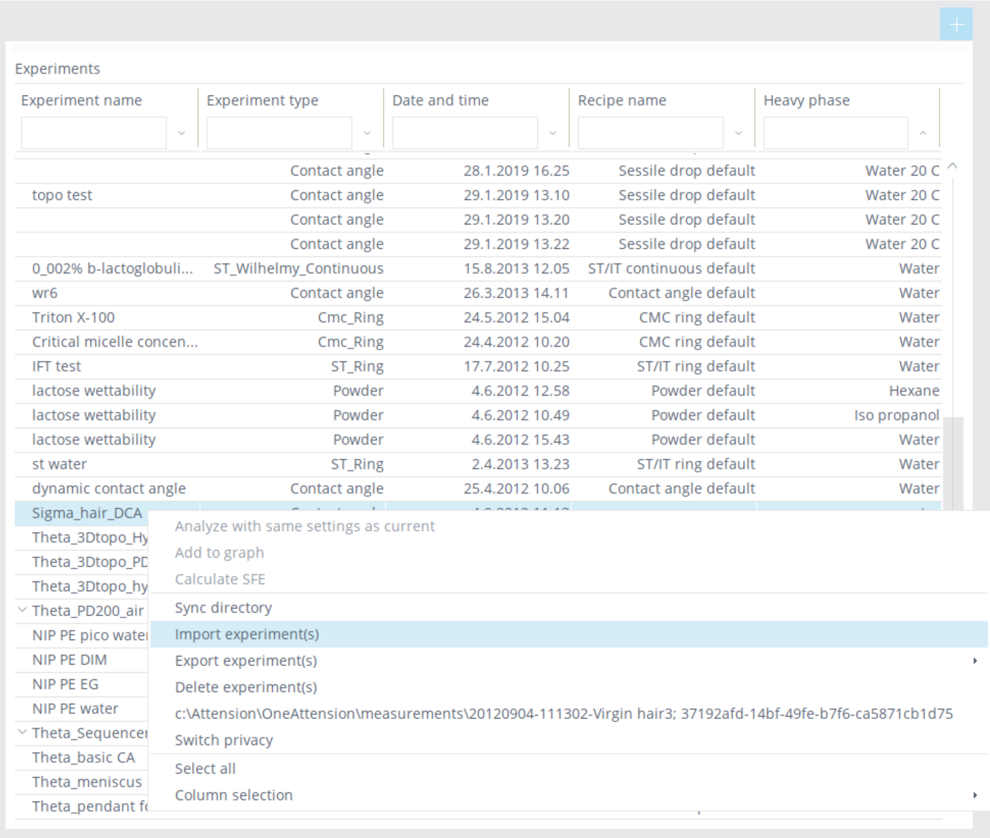
4.3 Analysis tab

After an experiment has been performed, you can return to the data for further analysis on **Analysis tab**. Click the + sign on top right corner to open up the list of experiments and select the experiment you would like to analyze by double-clicking it. Different kinds of filter options are located in the upper part of the **Analysis tab**, such as experiment name and type, date and time, and username. These may help to find the preferred experiment.



Experiment name	Experiment type	Date and time	Recipe name	Heavy phase
Theta_3Dtopo_Hydrop...	Contact angle	29.8.2013 12.54	Sessile drop default	Water
Theta_3Dtopo_PDMS	Contact angle	14.8.2013 11.24	Sessile drop default	Water
Theta_3Dtopo_hydrop...	Contact angle	3.10.2013 14.22	Sessile drop default	Water
Theta_PD200_air in SDS	Pulsating drop	7.11.2011 12.56	air in SDS	water
NIP PE pico water	Contact angle	30.1.2012 11.35	NIP pico	
NIP PE DIM	Contact angle	3.1.2012 16.15	NIP recipe	Di-iodomethane
NIP PE EG	Contact angle	3.1.2012 12.45	Sessile drop default	Ethylene glycol
NIP PE water	Contact angle	3.1.2012 10.33	Sessile drop default	Water
Theta_Sequencer_CA	Contact angle	21.12.2012 13.00		
Theta_basic CA	Contact angle	25.11.2011 15.11		water
Theta_meniscus	Meniscus	22.5.2012 13.21		
Theta_pendant for wa...	Surface tension	3.5.2011 15.41	pendant	Water
Theta_reverse pendant	Surface tension	17.11.2011 12.52	Reverse pendant	Water
	Pulsating drop	29.1.2019 14.43	Pulsating drop default	Water 20 C
	Pulsating drop	29.1.2019 14.49	Pulsating drop default	Water 20 C
	Pulsating drop	29.1.2019 14.51	Pulsating drop default	Water 20 C
	Pulsating drop	29.1.2019 14.51	Pulsating drop default	Water 20 C
pendant test	Surface tension	29.1.2019 16.00	Pendant drop default	Water 20 C
	Surface tension	29.1.2019 16.01	Pendant drop default	Water 20 C
	Contact angle	29.1.2019 16.31	Sessile drop default	Water 20 C
	Contact angle	29.1.2019 16.37	Sessile drop default	Water 20 C
	Contact angle	29.1.2019 16.42	Sessile drop default	Water 20 C
	Contact angle	29.1.2019 16.50	Sessile drop default	Water 20 C
test dca	Dynamic contact angle	15.6.2018 13.20		
	Contact angle	31.1.2019 16.28	Sessile drop default	Water 20 C
	Contact angle	31.1.2019 16.29	Sessile drop default	Water 20 C
	Contact angle	31.1.2019 16.30	Sessile drop default	Water 20 C

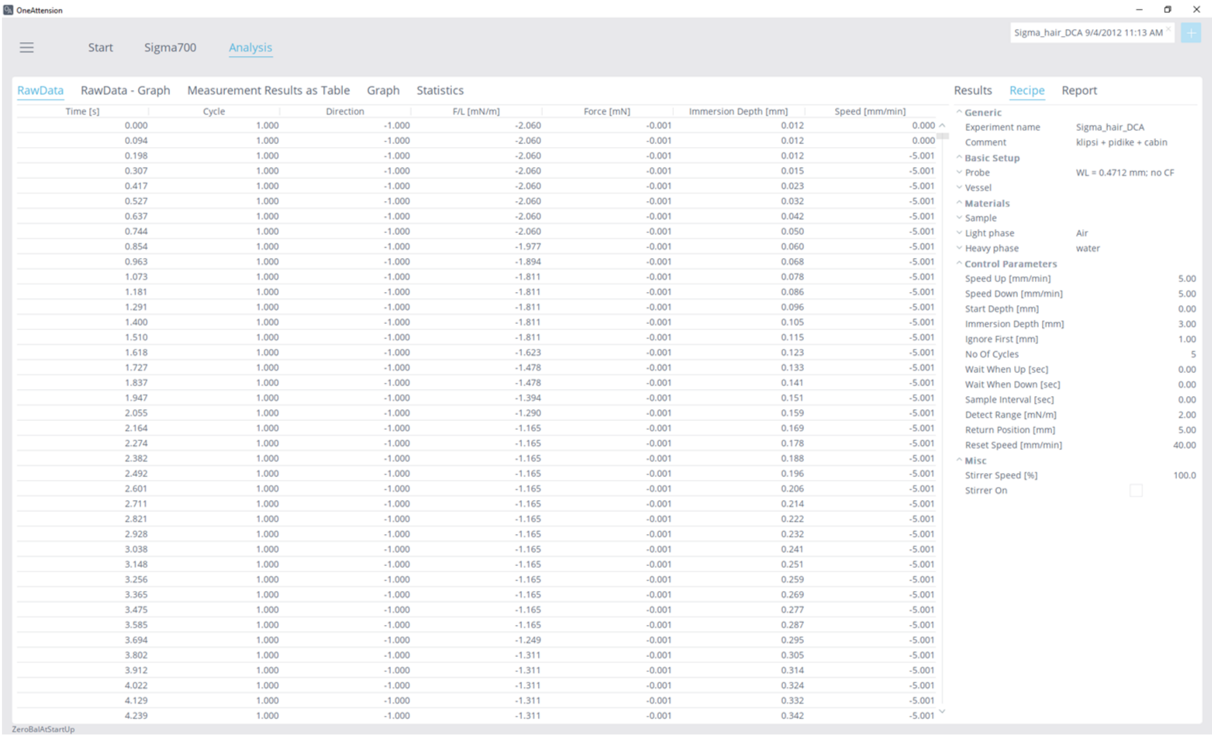
Right clicking on the experiment name on the list of experiments opens a pop-up menu, where you are able to Import or Export an experiment in OneAttension .bs or Excel (.xls/xlsx) format, among other options. You can also select multiple experiments and export them simultaneously. If you scan a barcode when the cursor is either in Experiment name or Recipe name field, only those experiments/recipes that match with the barcode are shown.



Experiments

Experiment name	Experiment type	Date and time	Recipe name	Heavy phase
	Contact angle	28.1.2019 16.25	Sessile drop default	Water 20 C
topo test	Contact angle	29.1.2019 13.10	Sessile drop default	Water 20 C
	Contact angle	29.1.2019 13.20	Sessile drop default	Water 20 C
	Contact angle	29.1.2019 13.22	Sessile drop default	Water 20 C
0_002% b-lactoglobuli...	ST_Wilhelmy_Continuous	15.8.2013 12.05	ST/IT continuous default	Water
wr6	Contact angle	26.3.2013 14.11	Contact angle default	Water
Triton X-100	Cmc_Ring	24.5.2012 15.04	CMC ring default	Water
Critical micelle concen...	Cmc_Ring	24.4.2012 10.20	CMC ring default	Water
IFT test	ST_Ring	17.7.2012 10.25	ST/IT ring default	Water
lactose wettability	Powder	4.6.2012 12.58	Powder default	Hexane
lactose wettability	Powder	4.6.2012 10.49	Powder default	Iso propanol
lactose wettability	Powder	4.6.2012 15.43	Powder default	Water
st water	ST_Ring	2.4.2013 13.23	ST/IT ring default	Water
dynamic contact angle	Contact angle	25.4.2012 10.06	Contact angle default	Water
Sigma_hair_DCA				
Theta_3Dtopo_Hy				
Theta_3Dtopo_PD				
Theta_3Dtopo_hy				
Theta_PD200_air				
NIP PE pico water				
NIP PE DIM				
NIP PE EG				
NIP PE water				
Theta_Sequencer				
Theta_basic CA				
Theta_meniscus				
Theta_pendant fo				

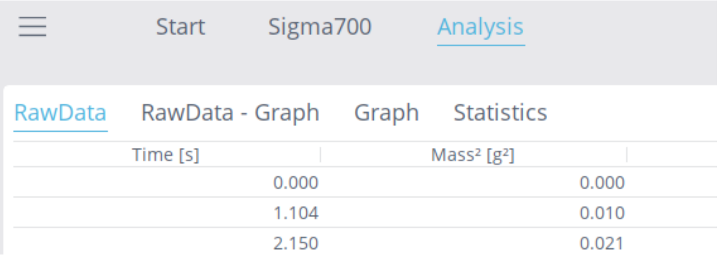
After you have selected the experiment you desire, the data for that experiment will be displayed.



Time [s]	Cycle	Direction	F/L [mN/m]	Force [mN]	Immersion Depth [mm]	Speed [mm/min]
0.000	1.000	-1.000	-2.060	-0.001	0.012	0.000
0.094	1.000	-1.000	-2.060	-0.001	0.012	0.000
0.198	1.000	-1.000	-2.060	-0.001	0.012	-5.001
0.307	1.000	-1.000	-2.060	-0.001	0.015	-5.001
0.417	1.000	-1.000	-2.060	-0.001	0.023	-5.001
0.527	1.000	-1.000	-2.060	-0.001	0.032	-5.001
0.637	1.000	-1.000	-2.060	-0.001	0.042	-5.001
0.744	1.000	-1.000	-2.060	-0.001	0.050	-5.001
0.854	1.000	-1.000	-1.977	-0.001	0.060	-5.001
0.963	1.000	-1.000	-1.894	-0.001	0.068	-5.001
1.073	1.000	-1.000	-1.811	-0.001	0.078	-5.001
1.181	1.000	-1.000	-1.811	-0.001	0.086	-5.001
1.291	1.000	-1.000	-1.811	-0.001	0.096	-5.001
1.400	1.000	-1.000	-1.811	-0.001	0.105	-5.001
1.510	1.000	-1.000	-1.811	-0.001	0.115	-5.001
1.618	1.000	-1.000	-1.623	-0.001	0.123	-5.001
1.727	1.000	-1.000	-1.478	-0.001	0.133	-5.001
1.837	1.000	-1.000	-1.478	-0.001	0.141	-5.001
1.947	1.000	-1.000	-1.394	-0.001	0.151	-5.001
2.055	1.000	-1.000	-1.290	-0.001	0.159	-5.001
2.164	1.000	-1.000	-1.165	-0.001	0.169	-5.001
2.274	1.000	-1.000	-1.165	-0.001	0.178	-5.001
2.382	1.000	-1.000	-1.165	-0.001	0.188	-5.001
2.492	1.000	-1.000	-1.165	-0.001	0.196	-5.001
2.601	1.000	-1.000	-1.165	-0.001	0.206	-5.001
2.711	1.000	-1.000	-1.165	-0.001	0.214	-5.001
2.821	1.000	-1.000	-1.165	-0.001	0.222	-5.001
2.928	1.000	-1.000	-1.165	-0.001	0.232	-5.001
3.038	1.000	-1.000	-1.165	-0.001	0.241	-5.001
3.148	1.000	-1.000	-1.165	-0.001	0.251	-5.001
3.256	1.000	-1.000	-1.165	-0.001	0.259	-5.001
3.365	1.000	-1.000	-1.165	-0.001	0.269	-5.001
3.475	1.000	-1.000	-1.165	-0.001	0.277	-5.001
3.585	1.000	-1.000	-1.165	-0.001	0.287	-5.001
3.694	1.000	-1.000	-1.249	-0.001	0.295	-5.001
3.802	1.000	-1.000	-1.311	-0.001	0.305	-5.001
3.912	1.000	-1.000	-1.311	-0.001	0.314	-5.001
4.022	1.000	-1.000	-1.311	-0.001	0.324	-5.001
4.129	1.000	-1.000	-1.311	-0.001	0.332	-5.001
4.239	1.000	-1.000	-1.311	-0.001	0.342	-5.001

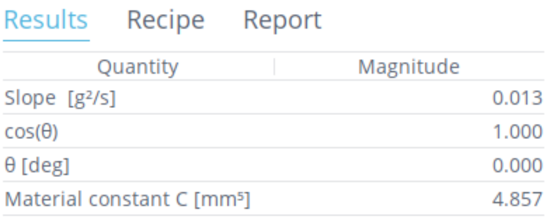
Generic	
Experiment name	Sigma_hair_DCA
Comment	klipsi + pidike + cabin
Basic Setup	
Probe	WL = 0.4712 mm; no CF
Vessel	
Materials	
Sample	
Light phase	Air
Heavy phase	water
Control Parameters	
Speed Up [mm/min]	5.00
Speed Down [mm/min]	5.00
Start Depth [mm]	0.00
Immersion Depth [mm]	3.00
Ignore First [mm]	1.00
No Of Cycles	5
Wait When Up [sec]	0.00
Wait When Down [sec]	0.00
Sample Interval [sec]	0.00
Detect Range [mN/m]	2.00
Return Position [mm]	5.00
Reset Speed [mm/min]	40.00
Misc	
Stirrer Speed [%]	100.0
Stirrer On	☐

Raw data, graph settings and statistics settings are available at top of the experiment data window.



Time [s]	Mass^2 [g^2]
0.000	0.000
1.104	0.010
2.150	0.021

Top right part of the experiment data window contains measurement results table, the recipe tab report tab. It can be helpful to edit the recipe at this point if you wish to recalculate the data produced based on new information about the materials involved. Report tab allows you to generate a report of the experiment. You are able to choose the report content.



Quantity	Magnitude
Slope [g^2/s]	0.013
$\cos(\theta)$	1.000
θ [deg]	0.000
Material constant C [mm^5]	4.857

Right clicking the measurement data opens a pop-up menu with the following options:

Select all: Selects all the data

Copy selected: Copies the selected data for use in some other program

Copy all: Copies all the data from the current experiment

Export all: Will export all the data of the current experiment. The software will give you the option to name the data file and format (.csv, .txt, .xls) to save as you like.

Column selection: Enables you to choose the measurement parameters which are shown in the experiment data table. The option depends on the measurement type.

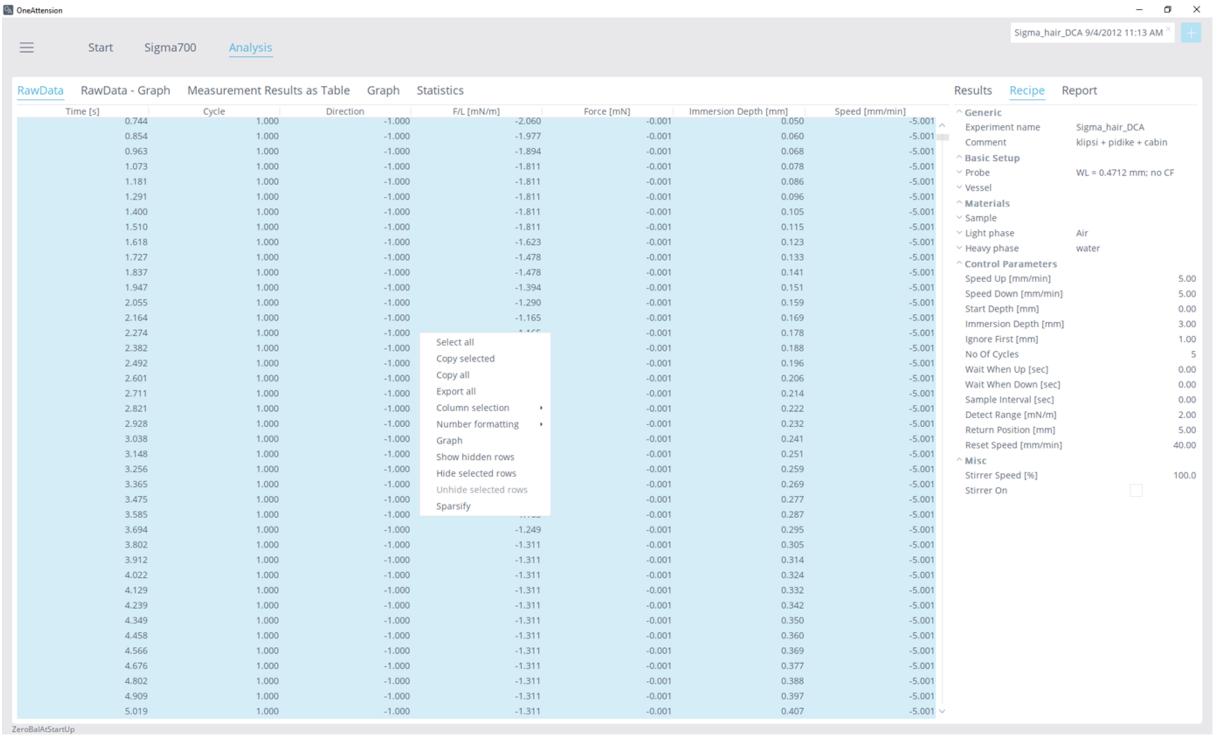
Number formatting: Enable you to choose the format of the digits shown in the experiment data table.

Graph: Allows you to draw a graph with the selected values. When right clicking on a graph, the software allows you to change the properties of the graph, copy the graph, save the graph as a picture, print the graph, zoom in and out and autorange.

Hide selected rows: Enable to hide the selected row(s). The hidden rows will not be included in the further analyses or graphs.

Show hidden rows: Enables to return the hidden rows.

Sparsify: In case the number of data points need to be reduced the Sparsifier window will able to choose every Nth data point to be hidden or kept.



Time [s]	Cycle	Direction	F/L [mN/m]	Force [mN]	Immersion Depth [mm]	Speed [mm/min]
0.744	1.000	-1.000	-2.060	-0.001	0.050	-5.001
0.854	1.000	-1.000	-1.977	-0.001	0.060	-5.001
0.963	1.000	-1.000	-1.894	-0.001	0.068	-5.001
1.073	1.000	-1.000	-1.811	-0.001	0.078	-5.001
1.181	1.000	-1.000	-1.811	-0.001	0.086	-5.001
1.291	1.000	-1.000	-1.811	-0.001	0.096	-5.001
1.400	1.000	-1.000	-1.811	-0.001	0.105	-5.001
1.510	1.000	-1.000	-1.811	-0.001	0.115	-5.001
1.618	1.000	-1.000	-1.623	-0.001	0.123	-5.001
1.727	1.000	-1.000	-1.478	-0.001	0.133	-5.001
1.837	1.000	-1.000	-1.478	-0.001	0.141	-5.001
1.947	1.000	-1.000	-1.394	-0.001	0.151	-5.001
2.055	1.000	-1.000	-1.290	-0.001	0.159	-5.001
2.164	1.000	-1.000	-1.165	-0.001	0.169	-5.001
2.274	1.000	-1.000	[illegible]	-0.001	0.178	-5.001
2.382	1.000	-1.000	[illegible]	-0.001	0.188	-5.001
2.492	1.000	-1.000	[illegible]	-0.001	0.196	-5.001
2.601	1.000	-1.000	[illegible]	-0.001	0.206	-5.001
2.711	1.000	-1.000	[illegible]	-0.001	0.214	-5.001
2.821	1.000	-1.000	[illegible]	-0.001	0.222	-5.001
2.928	1.000	-1.000	[illegible]	-0.001	0.232	-5.001
3.038	1.000	-1.000	[illegible]	-0.001	0.241	-5.001
3.148	1.000	-1.000	[illegible]	-0.001	0.251	-5.001
3.256	1.000	-1.000	[illegible]	-0.001	0.259	-5.001
3.365	1.000	-1.000	[illegible]	-0.001	0.269	-5.001
3.475	1.000	-1.000	[illegible]	-0.001	0.277	-5.001
3.585	1.000	-1.000	[illegible]	-0.001	0.287	-5.001
3.694	1.000	-1.000	-1.249	-0.001	0.295	-5.001
3.802	1.000	-1.000	-1.311	-0.001	0.305	-5.001
3.912	1.000	-1.000	-1.311	-0.001	0.314	-5.001
4.022	1.000	-1.000	-1.311	-0.001	0.324	-5.001
4.129	1.000	-1.000	-1.311	-0.001	0.332	-5.001
4.239	1.000	-1.000	-1.311	-0.001	0.342	-5.001
4.349	1.000	-1.000	-1.311	-0.001	0.350	-5.001
4.458	1.000	-1.000	-1.311	-0.001	0.360	-5.001
4.566	1.000	-1.000	-1.311	-0.001	0.369	-5.001
4.676	1.000	-1.000	-1.311	-0.001	0.377	-5.001
4.802	1.000	-1.000	-1.311	-0.001	0.388	-5.001
4.909	1.000	-1.000	-1.311	-0.001	0.397	-5.001
5.019	1.000	-1.000	-1.311	-0.001	0.407	-5.001

Generic

Experiment name	Sigma_hair_DCA
Comment	klipsi + pidike + cabin

Basic Setup

Probe	WL = 0.4712 mm; no CF
Vessel	

Materials

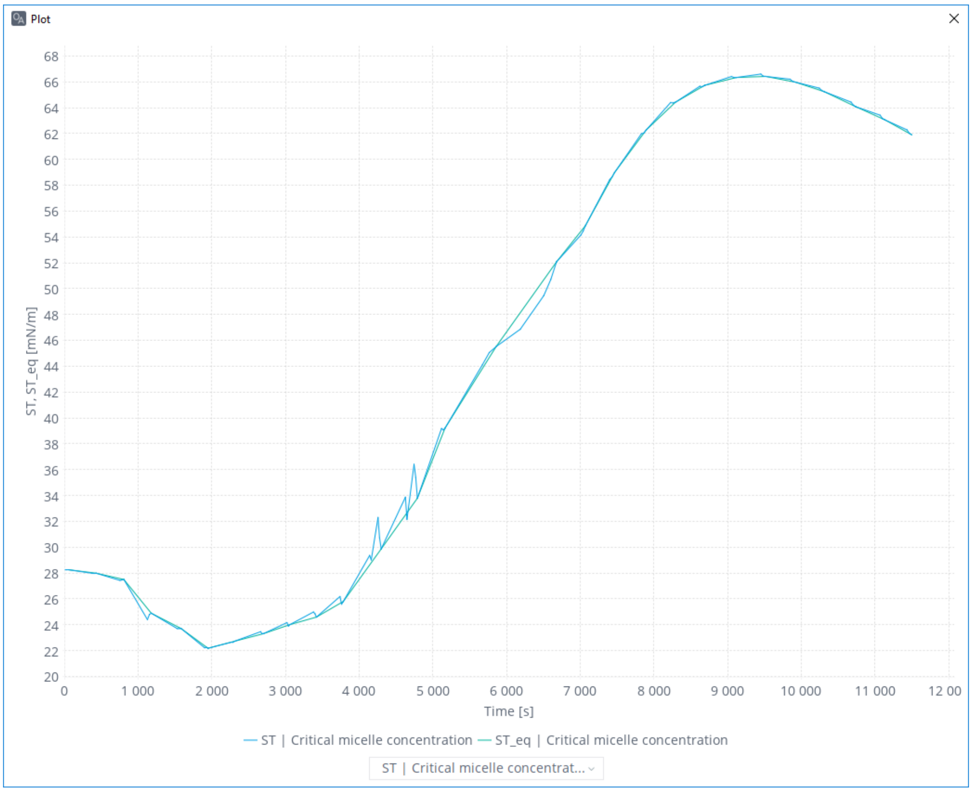
Sample	
Light phase	Air
Heavy phase	water

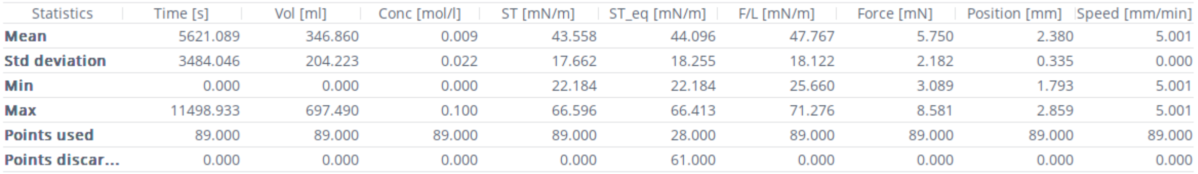
Control Parameters

Speed Up [mm/min]	5.00
Speed Down [mm/min]	5.00
Start Depth [mm]	0.00
Immersion Depth [mm]	3.00
Ignore First [mm]	1.00
No Of Cycles	5
Wait When Up [sec]	0.00
Wait When Down [sec]	0.00
Sample Interval [sec]	0.00
Detect Range [mN/m]	2.00
Return Position [mm]	5.00
Reset Speed [mm/min]	40.00

Misc

Stirrer Speed [%]	100.0
Stirrer On	☐

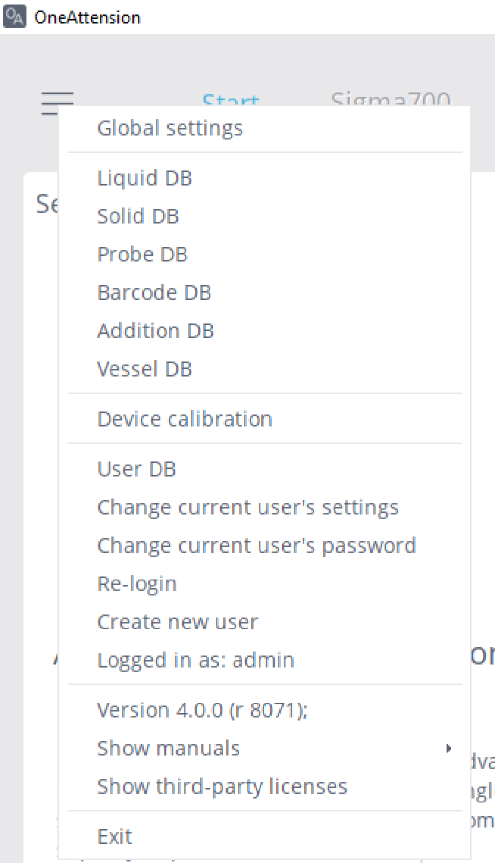




Statistics	Time [s]	Vol [ml]	Conc [mol/l]	ST [mN/m]	ST_eq [mN/m]	F/L [mN/m]	Force [mN]	Position [mm]	Speed [mm/min]
Mean	5621.089	346.860	0.009	43.558	44.096	47.767	5.750	2.380	5.001
Std deviation	3484.046	204.223	0.022	17.662	18.255	18.122	2.182	0.335	0.000
Min	0.000	0.000	0.000	22.184	22.184	25.660	3.089	1.793	5.001
Max	11498.933	697.490	0.100	66.596	66.413	71.276	8.581	2.859	5.001
Points used	89.000	89.000	89.000	89.000	28.000	89.000	89.000	89.000	89.000
Points discar...	0.000	0.000	0.000	0.000	61.000	0.000	0.000	0.000	0.000

4.4 Main menu

You can open the main menu from top left corner of the window. The menu provides access to all application settings, including liquid, solid, probe, barcode, user, addition and vessel databases as well as global settings and device calibration window. From the menu you can also change current user's settings and password and create new user accounts. In addition, by clicking "Show manuals" you are able to access your instrument manuals.



Global settings: In this part of the software, you are able select the path where your experiments are saved, choose user language (English/Chinese), as well as choose the additional hardware you are using (see figure below).

Liquid database: Database for creating and editing probe liquid alternatives for recipes.

Solid database: Database for creating and editing solid material alternatives for recipes.

Probe database: Database for creating and editing Sigma force tensiometer probe alternatives for recipes. Not utilized with Theta optical tensiometers.

Barcode database: Database for creating and editing barcodes to quickly open experiment recipes with optional barcode scanner.

Addition database: Database for creating and editing addition alternatives for recipes. This section is mainly related to Sigma force tensiometer measurements.

Vessel database: Database for creating and editing vessel alternatives for recipes. This section is mainly related to Sigma force tensiometer measurements.

Systems diagnostics/ Device calibration: Function for analyzing the communication between devices and computer as well as for the calibration of devices. Can be activated by selecting **Device calibration** on the main menu.

User settings in the main menu will allow managing the user properties as follows:

User DB: Shows the list of all users. Operator level users can only use pre-defined recipes. Programmer level users are also able to modify and create new recipes. In addition to creating and modifying recipes, administrator level users can also manage other user accounts. From the database it is also possible to export and import user lists (.xls, txt or .csv file formats).

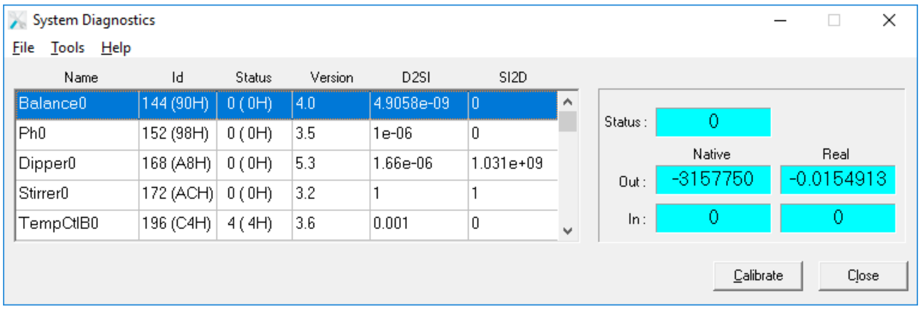
Change current user's settings: Enable to select the path for each user, where the measurements will be saved.

Change current user's password: The User is able to change her/his password.

Re-login: The other user is able to re-login in the system without shutting the program down.

Create new user: Administrator level users are able to create new users.

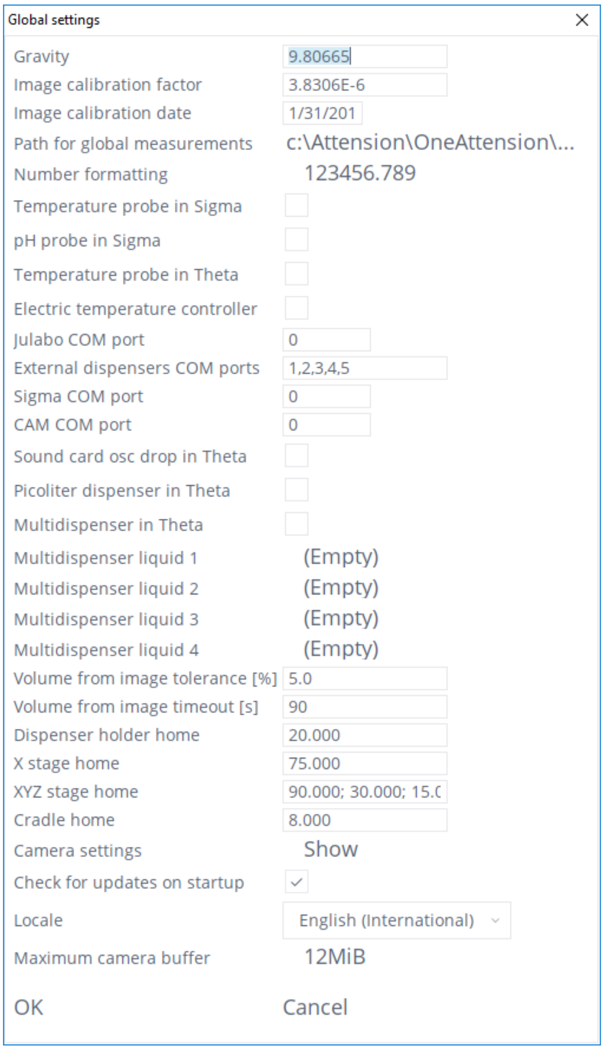
Logged in as: Will show the name of the current user.



Name	Id	Status	Version	D2SI	SI2D
Balance0	144 (90H)	0 (0H)	4.0	4.9058e-09	0
Ph0	152 (98H)	0 (0H)	3.5	1e-06	0
Dipper0	168 (A8H)	0 (0H)	5.3	1.66e-06	1.031e+09
Stirrer0	172 (ACH)	0 (0H)	3.2	1	1
TempCtlB0	196 (C4H)	4 (4H)	3.6	0.001	0

Status : 0

	Native	Real
Out :	-3157750	-0.0154913
In :	0	0



Global settings

Gravity	9.80665
Image calibration factor	3.8306E-6
Image calibration date	1/31/201
Path for global measurements	c:\Attension\OneAttension\...
Number formatting	123456.789
Temperature probe in Sigma	☐
pH probe in Sigma	☐
Temperature probe in Theta	☐
Electric temperature controller	☐
Julabo COM port	0
External dispensers COM ports	1,2,3,4,5
Sigma COM port	0
CAM COM port	0
Sound card osc drop in Theta	☐
Picoliter dispenser in Theta	☐
Multidispenser in Theta	☐
Multidispenser liquid 1	(Empty)
Multidispenser liquid 2	(Empty)
Multidispenser liquid 3	(Empty)
Multidispenser liquid 4	(Empty)
Volume from image tolerance [%]	5.0
Volume from image timeout [s]	90
Dispenser holder home	20.000
X stage home	75.000
XYZ stage home	90.000; 30.000; 15.
Cradle home	8.000
Camera settings	Show
Check for updates on startup	☑
Locale	English (International)
Maximum camera buffer	12MiB

4.4.1 Databases

There are several different databases in OneAttension. The meaning of these databases is explained below. Adding information to these databases is simple. Just open the database and right click on top of it and choose add. Different information is asked depending on the database. It is also possible to import data from Excel (.xls/xlsx) or comma-separated values (.csv) files to the database.

Liquid database: The information about liquids used in the measurements can be edited and added here. If you are using liquids, which are not available from the current default menu you may enter into this section to add new choices to the database. It is not required to fill in all the information fields, but you can fill just the ones you need for the measurements.

Solid database: The information about solids used in the measurements can be edited and added here. If you are using materials, which are not available from the current default menu you may enter into this section to add new choices to the database.

Probe database: The information about probes used in the measurements can be edited and added here. If you are using probes, which are not available from the current default menu you may enter into this section to add new choices to the database. You can also enter information of your samples used for dynamic contact angle measurements to this database.

Barcode database: Database for creating and editing barcodes to quickly open experiment recipes with optional barcode scanner.

User database: Contains the list of current user accounts. It is possible to edit the user information, e.g. password for the user or you can delete the user accounts.

Addition database: The information about additions used in the measurements can be edited and added here. If you are using additions, which are not available from the current default menu you may enter into this section to add new choices to the database. This can be useful for CMC measurements.

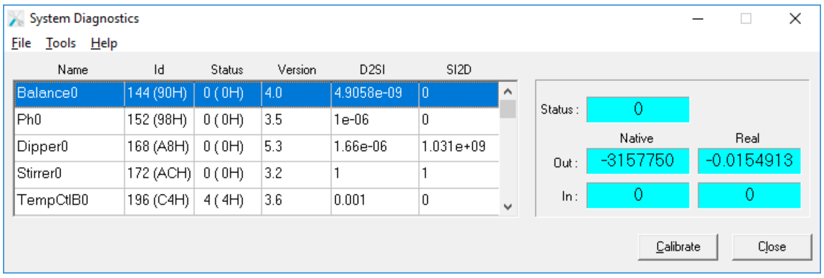
Vessel database: The information about vessels used in the measurements can be edited and added here. If you are using vessels, which are not available from the current default menu you may enter into this section to add new choices to the database.

4.4.2 Calibration of the balance

The best way to check if the calibration is correct and the balance is working is to zero the balance and place the calibration weight on the hook. The reading should be the same as the recorded calibration weight value (within ± 1.0 mg). If not, calibrate again. It is possible to test the balance also by measuring the surface tension of a liquid with known surface tension value. Notice however that water is not a good liquid for this purpose since it is easily contaminated and the surface tension then deviates from the literature value. Some solvents, like ethanol, are a better option.

Note also that there is no need to make the calibration of the instrument if the mass readings are correct. If you suspect that there is something wrong with the calibration, it is a good idea to first check (by following the above instructions), and then proceed to the calibration if needed.

Calibration of the Sigma 700/701 should be done before the first measurement, or whenever the Sigma has been moved or unused for a long time. The calibration is done by opening Device calibration window from the main menu or **Start tab** in OneAttension Select the balance and click calibrate.



Name	Id	Status	Version	D2SI	SI2D
Balance0	144 (90H)	0 (0H)	4.0	4.9058e-09	0
Ph0	152 (98H)	0 (0H)	3.5	1e-06	0
Dipper0	168 (A8H)	0 (0H)	5.3	1.66e-06	1.031e+09
Stirrer0	172 (ACH)	0 (0H)	3.2	1	1
TempCtlB0	196 (C4H)	4 (4H)	3.6	0.001	0

Status : 0

	Native	Real
Out :	-3157750	-0.0154913
In :	0	0

For Sigma 700, the calibration is done automatically when “Calibrate” is pressed.

For Sigma 701, the following steps of the four-point calibration should be performed:

1) Fill in the masses of the three calibration weights in the software. The masses are written on the plastic bag containing the calibration weights. Note that the mass of the first point is zero.

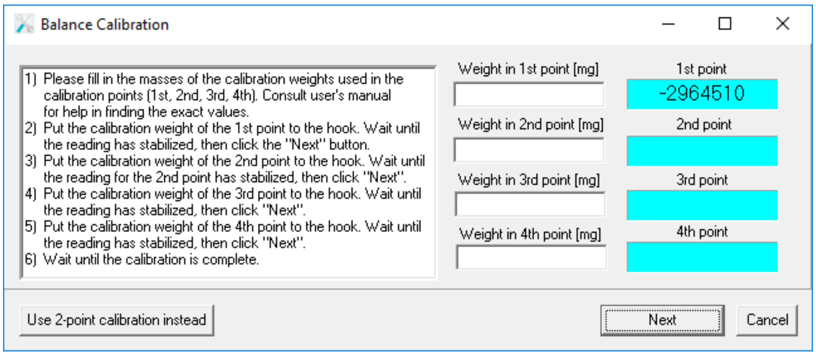
2) Make sure that the hook is not moving and click the “Next” button.

3) Place the calibration weight of the second point on the hook and wait until you can see that the hook is not moving anymore. Then click the “Next” button.

4) Remove the calibration weight of the second point from the hook, put the calibration weight of the third point on the hook, and wait until the hook is not moving. Then click the “Next” button.

5) Remove the calibration weight of the third point from the hook, put the calibration weight of the fourth point on the hook, and wait until the hook is not moving. Then click the “Next” button.

6) Wait until the calibration is complete. When calibration is done for the first time, it can take several minutes.



1) Please fill in the masses of the calibration weights used in the calibration points (1st, 2nd, 3rd, 4th). Consult user's manual for help in finding the exact values.
2) Put the calibration weight of the 1st point to the hook. Wait until the reading has stabilized, then click the "Next" button.
3) Put the calibration weight of the 2nd point to the hook. Wait until the reading for the 2nd point has stabilized, then click "Next".
4) Put the calibration weight of the 3rd point to the hook. Wait until the reading has stabilized, then click "Next".
5) Put the calibration weight of the 4th point to the hook. Wait until the reading has stabilized, then click "Next".
6) Wait until the calibration is complete.

1st point: -2964510

The four-point calibration is the recommended calibration procedure for Sigma 701, as it calibrates the balance over the whole measurement range. However, it is also possible to use the two-point calibration. For the 2-point calibration, the following steps should be performed:

1) Write the mass of the calibration weight in the software. The mass is written on the plastic bag containing the calibration weight.

2) Place a Wilhelmy plate or a Du Noüy ring on the hook.

3) Wait the balance reading to stabilize. At least the first 3 digits should be stable before continuing. Press next.

4) Place the calibration weight of known mass on the hook (leave the Wilhelmy plate / Du Noüy ring there too). The mass of the calibration weight should be around 2 g.

5) Wait again for the reading to stabilize and press calibrate. The system starts calculating a new calibration value. When calibration is done for the first time, it can take several minutes.

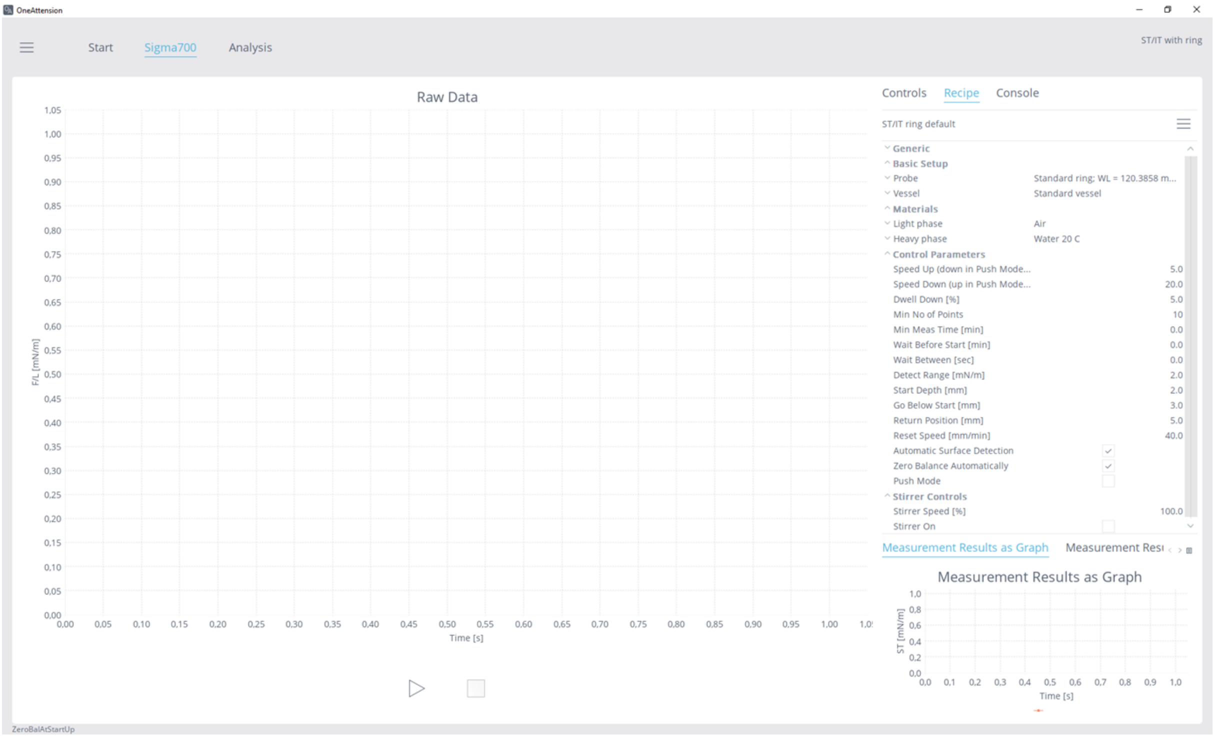
5 Surface and interfacial tension measurements

To perform a measurement of Surface/Interfacial Tension with your Sigma you must first prepare your physical setup and software. For best results, the Sigma main unit should be switched on for at least 24 hours before measurement. Make sure your measuring vessel is thoroughly cleaned. Your probe used for the surface tension measurement, i.e. Wilhelmy plate or Du Noüy ring, should be cleaned with solvents and flamed prior to use. To flame clean your probe, be sure you have a strong flame source, comparable to a bunsen burner (Temperature > 1000 ºC). Low heat flames will leave residue on your probe, which will cause significant error. Hold the probe in the hottest part of the flame until the entire lower section glows brightly. This should only take a few seconds.

At this point it is advisable to drive the stage meant for holding the liquid vessel to its lowest position by using the Manual Membrane Keyboard ↓ button. Then fill your vessel with the liquid and place it on the stage. Hereafter, hang the cleaned probe on the balance hook.

To proceed with the preparations of the measurement choose the surface/interfacial tension measurement icon on the **Start tab**. The software will allow you to choose whether you would like to conduct the measurement with a Du Noüy ring or with Wilhelmy plate. Click the option you want.

5.1 Du Noüy ring measurement



ST/IT ring default

Generic
Basic Setup
Probe: Standard ring; WL = 120.3858 m...
Vessel: Standard vessel
Materials
Light phase: Air
Heavy phase: Water 20 C
Control Parameters
Speed Up (down in Push Mode...: 5.0
Speed Down (up in Push Mode...: 20.0
Dwell Down [%]: 5.0
Min No of Points: 10
Min Meas Time [min]: 0.0
Wait Before Start [min]: 0.0
Wait Between [sec]: 0.0
Detect Range [mN/m]: 2.0
Start Depth [mm]: 2.0
Go Below Start [mm]: 3.0
Return Position [mm]: 5.0
Reset Speed [mm/min]: 40.0
Automatic Surface Detection ☑
Zero Balance Automatically ☑
Push Mode ☐
Stirrer Controls
Stirrer Speed [%]: 100.0
Stirrer On ☐

The Du Noüy ring recipe contains the following fields (in addition to generic field)

Basic setup

Probe: Here the details of the selected probe are listed. The probe can be selected from the database or the dimensions can be given manually. WL stands for “wetted length” and CF for “correction file”

Name: Name of the probe e.g. Standard ring.

Type: Type of the probe can be selected from the list, for ring “Round ring” is selected.

R (or plate width) [mm]: The radius of the Du Noüy ring.

r (or plate thickness) [mm]: The radius of the Du Noüy ring wire.

Correction file: For measurements with the Du Noüy ring, the correction file is needed. Read more information about the correction file from the Theory chapter of this manual.

Vessel: Details of the used vessel are listed here (not mandatory information for surface and interfacial tension measurements). Vessel can be chosen from the database or given manually.

Name: Name of the vessel, e.g. Standard vessel.

Diameter [mm]: The diameter of the vessel.

Volume [ml]: The volume of the vessel.

Materials

Light Phase: The information about the light phase is listed here in details. The light phase can be chosen from the list or the information can be written. In case of surface tension measurements, the light phase is air. In interfacial tension measurements the light phase is the liquid on top. Not all the information need to be filled in. When measurements are done by using the Du Noüy ring, the density of the light phase has to be known since it is utilized in correction file.

Name: Name of the light phase, e.g. air.

γ^{tot}: Total surface tension.

γ^{d}: Dispersive component of the surface tension.

γ^{+}: Base component of the surface tension.

γ^{-}: Acid component of the surface tension

ρ: Density

η: Viscosity

Temperature [°C]: Temperature at which the parameters are defined.

Molecular weight [g/mol]: Molecular weight

Heavy Phase: The information about the heavy phase is listed here in details. In case of surface tension measurements, the heavy phase is the liquid that is measured. The density of the heavy phase has to be known when Du Noüy ring is used. The parameters are as listed above for the light phase.

Control Parameters

Speed Up: Speed at which probe moves during withdrawal

Speed Down: Speed at which probe moves during immersion

Dwell Down [%]: Amount of drop in F/L (in % from maximum measure value) between each measurement cycle or pull. When the surface tension is really low, it might be useful to increase this values.

Min No Points: Minimum number of surface tension values which will be measured

Min Meas Time: Minimum amount of time for which the experiment will run

Wait before start: The software waits a defined amount of time before starting the experiment.

Wait between: Wait time in between the measurements

Detect range: Amount of change in force, which will register as contact with interface. If the liquid interface is detected before the actual contact of the probe has taken place, this value is set too low. If the surface is not detected, this value is set too high.

Start depth: The depth from where the experiment is started.

Go below start: Probe is immersed lower than the starting position.

Return position: The position where the probe is returned to after the experiment.

Reset speed: The speed of the probe when not doing an experiment but controlling the probe manually.

Automatic surface detection: When selected the balance is automatically zeroed when start button is pressed and the position is zeroed at the surface.

Zero Balance Automatically: When selected the balance is automatically zeroed at the start of measurement.

Push Mode: When selected an interfacial tension measurement is done in Push mode, that is the ring is pushed down in the heavy phase. When Push Mode is selected, Automatic surface detection is always unselected.

Misc

Stirrer speed [%]: The percentage from maximum stirrer speed. 100 % is the full speed.

Stirrer on: When selected the magnetic stirring is on.

5.1.1 Instructions for surface tension measurements with Du Noüy ring

1. Fill in the empty fields in the default recipe or open a previously stored recipe. At least following fields should be checked.
    - Experiment name
    - Check that the probe dimensions are correct
    - Check that light phase is air
    - Heavy phase is the liquid you are measuring (liquid can be chosen from the database or the properties can be given manually).
2. Fill the beaker with the liquid you want to measure, clean the probe and hang it on the hook. Bring the probe close to surface to save some measurement time, and press start.
3. The instrument will show the measured force/wetted length in real time and plot the corrected surface tension values in the graph. Both measured and corrected values will also be shown in the table format.
4. The device will make as many repeated measurements as indicated in the recipe (10 in the default recipe), and stop after the measurement is completed or the stop button is pressed.

5.1.2 Instructions for interfacial tension measurements with Du Noüy ring

The interfacial tension measurement is done by using the same measurement type as with the surface tension measurements.

1. Fill in the empty fields in the default recipe or open a previously stored recipe. At least the following fields should be checked.
    - Experiment name
    - Check that the probe dimensions are correct

    - Put the less dense liquid as light phase (liquid can be chosen from the database or the properties can be given manually)
    - Put the denser liquid as heavy phase (usually water)
    - Unmark the "automatic surface detection"
2. Fill the beaker with the heavy liquid. Clean and hang the probe.
3. Lower the probe so that it is immersed in the liquid.
4. Pour the less dense liquid on top.
5. Bring the probe close to the interface but keep it still in the heavy phase.
6. Press start.

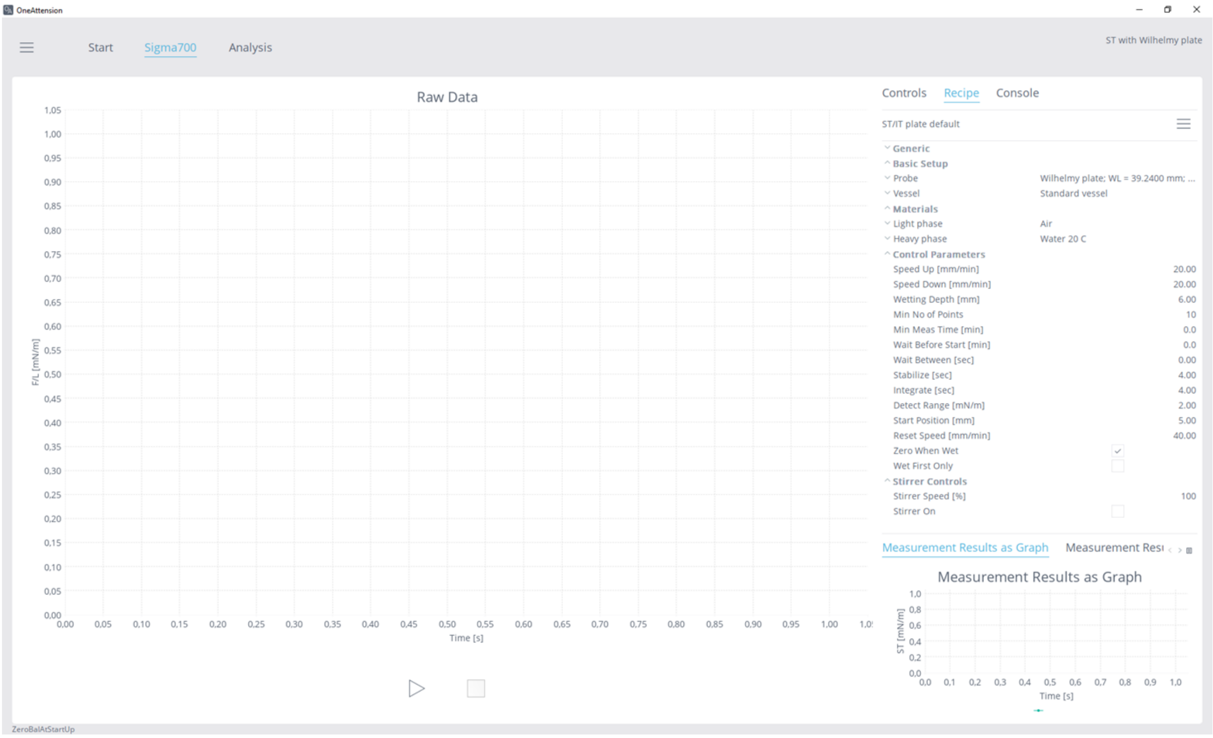
Note! Interfacial tension measurements should always be done from polar to non-polar liquid. Most often measurements can be done as described above since in interfacial tension measurement between polar and non-polar liquid, the polar is almost always the heavier one.

Instructions for interfacial tension measurements with Du Noüy ring in Push Mode

Using Push Mode, it is possible to measure interfacial tension between liquids where the non-polar liquid is the heavier liquid. The measurement is done with a Du Noüy ring that has an additional weight attached to the ring body. In the "push mode" measurement the ring is pushed down to the heavy phase, as opposed to lifting it up to the light phase.

1. Fill in the empty fields in the default recipe or open a previously stored recipe. At least the following fields should be checked.
    - Experiment name
    - Check that the probe dimensions are correct
    - Put the less dense liquid as light phase (liquid can be chosen from the database or the properties can be given manually)
    - Put the denser liquid as heavy phase
    - Check "Push mode"
2. Pour the heavy liquid in the beaker.
3. Pour the less dense liquid on top.
4. Clean and hang the probe.
5. Lower the probe so that it is immersed in the light phase. Lower the probe so that it is at a height that is approximately the "Start depth" above the interface.
6. Press start.

5.2 Wilhelmy plate measurements



ST/IT plate default

Generic	
Basic Setup	
Probe	Wilhelmy plate; WL = 39.2400 mm; ...
Vessel	Standard vessel
Materials	
Light phase	Air
Heavy phase	Water 20 C
Control Parameters	
Speed Up [mm/min]	20.00
Speed Down [mm/min]	20.00
Wetting Depth [mm]	6.00
Min No of Points	10
Min Meas Time [min]	0.0
Wait Before Start [min]	0.0
Wait Between [sec]	0.00
Stabilize [sec]	4.00
Integrate [sec]	4.00
Detect Range [mN/m]	2.00
Start Position [mm]	5.00
Reset Speed [mm/min]	40.00
Zero When Wet	☑
Wet First Only	☐
Stirrer Controls	
Stirrer Speed [%]	100
Stirrer On	☐

Another method for surface and interfacial tension measurements is the use of Wilhelmy plate. In principle Wilhelmy plate and Du Noüy ring should lead to same surface/interfacial tension values. Wilhelmy plate is thought to work better with high viscous liquids.

The Wilhelmy plate recipe contains the following field (in addition to generic field):

Basic setup

Probe: Here the details of the selected probe are listed. The probe can be selected from the database or the dimensions can be given manually. WL stands for "wetted length" and CF for "correction file".

Name: Name of the probe e.g. Wilhelmy plate.

Type: Type of the probe can be selected from the list, for Wilhelmy plate "Regtangular plate" is selected.

R (or plate width) [mm]: Width of the Wilhelmy plate.

r (or plate thickness) [mm]: Thickness of the Wilhelmy plate.

Correction file: Correction file is not used with Wilhelmy plate

Light Phase Buoyancy compensation [mN] (only available in IT measurement): The compensation factor for the light phase buoyancy in IT measurements.

Vessel: Details of the used vessel are listed here (not mandatory information for surface and interfacial tension measurements). Vessel can be chosen from the database or given manually.

Name: Name of the vessel, e.g. Standard vessel.

Diameter [mm]: The diameter of the vessel.

Volume [ml]: The volume of the vessel.

Materials

Light Phase: The information about the light phase is listed here in details. The light phase can be chosen from the list or the information can be written. In case of surface tension measurements, the light phase is air. In interfacial tension measurements the light phase is the liquid on top. These informations are not required for the measurements.

Name: Name of the light phase, e.g. air.

γ^{tot}: Total surface tension.

γ^{d}: Dispersive component of the surface tension.

γ^{+}: Base component of the surface tension.

γ^{-}: Acid component of the surface tension

ρ: Density

η: Viscosity

Temperature [°C]: Temperature at which the parameters are defined.

Molecular weight [g/mol]: Molecular weight

Heavy Phase: The information about the heavy phase is listed here in details. In case of surface tension measurements, the heavy phase is the liquid that is measured. This information is not required for the Wilhelmy plate measurement.

Control Parameters

Check buoyancy in light phase (only available in IT measurement): Is used for measuring the buoyancy factor for the light phase in IT measurements

Speed Up: Speed at which probe moves during withdrawal

Speed Down: Speed at which probe moves during immersion

Wetting depth: The depth to which the plate is immersed

Min No Points: Minimum number of surface tension values which will be measured

Min Meas Time: Minimum amount of time for which the experiment will run

Wait before start: The software waits a defined amount of time before starting the experiment.

Wait between: Wait time in between the measurements

Stabilize [sec]: Time to wait before starting to collect data. There should be some waiting time

Integrate [sec]: Time during which the data is collected (results is an average over this time period). Reduce noise.

Detect range: Amount of change in force, which will register as contact with interface. If the liquid interface is detected before the actual contact of the probe has taken place, this value is set too low. If the surface is not detected, this value is set too high.

Start position: Position above interface to which the probe will return in between the measurements.

Reset speed: The speed of the probe when not doing an experiment but controlling the probe manually.

Zero When Wet: Zero the balance after wetting the probe.

Wet First Only: When active, the probe is wetted only once before the measurements. When inactive, the probe is wetted before each individual surface tension measurement.

Misc

Stirrer speed [%]: The percentage from maximum stirrer speed. 100 % is the full speed.

Stirrer on: When selected the magnetic stirring is on.

5.2.1 Instructions for surface tension measurements with Wilhelmy plate

1. Choose “ST with Wilhelmy plate” as the measurement method.
2. Fill in the empty fields in the default recipe or open a previously stored recipe. At least following fields should be checked.
3. Experiment name
4. Check that the probe dimensions are correct
5. Fill the beaker with the liquid you want to measure, clean the probe and hang it on the hook. Bring the probe close to surface to save some measurement time, and press start.
6. The instrument will show the measured force/wetted length in real time and plot the surface tension values in the graph. Results are also shown in table format.
7. The device will make as many repeated measurements as indicated in the recipe (10 in the default recipe), and stop automatically after the measurements are completed or the stop button is pressed.

5.2.2 Instructions for an interfacial tension measurement with Wilhelmy plate

1. Choose “IT with Wilhelmy plate” as the measurement method.
2. Choose “Check buoyancy in light phase” in the recipe.
3. Fill the beaker with the less dense liquid. Clean and hang the probe.
4. Raise the stage so that the plate is close to the liquid level but not touching it.
5. Press start. OneAttension will now measure the buoyancy factor for the light phase.
6. After measurement, check that the light phase buoyancy compensation in the basic setup has been updated.
7. Fill another beaker with the heavy liquid. Clean and hang the probe.
8. Raise the stage so that the plate is close to the liquid level but not touching it.
9. Fill in the empty fields in the default recipe or open a previously stored recipe. At least the following fields should be checked.
   - Experiment name
   - Check that the probe dimensions are correct
   - Select the appropriate measurement time, the time can be increase also during the measurement if needed.
10. Press start.
11. When the software asks you to, pour the less dense liquid on top.
12. Press ok.

If you are using the same light phase liquid for multiple measurements, the buoyancy factor doesn’t have to be measured separately each time. After measuring it once, you can insert the value manually to “Light Phase Buoyancy compensation”.

Note that amount of light phase has to be enough to keep the Wilhelmy plate immersed into the liquid throughout the whole measurement. There cannot be a situation where the Wilhelmy plate sees two interfaces (between heavy and light phase and between light phase and air).

5.3 Continuous Wilhelmy plate measurements

Apart from performing a standard Wilhelmy plate measurement it is also possible to make continuous Wilhelmy plate measurements. Instead of making several dips the plate is kept at the surface. This measurement type can be useful when surface tension value may vary as a function of time. The parameters in the Continuous Wilhelmy plate recipe are the same as in the standard Wilhelmy plate measurement, except that in the control parameters there is also a possibility to work manually.

5.3.1 Step by step instructions for a continuous Wilhelmy plate measurement

1. When clicking the surface tension measurement, the software will ask which method you want to use. Select "ST continuous Wilhelmy".
2. Fill in the empty fields in the recipe:
   - Experiment name
   - Check that the probe dimensions are correct
   - Select the appropriate measurement time, the time can be increase also during the measurement if needed.
3. Fill the beaker with the liquid you want to measure, clean to probe by flame and hang it on the hook. Bring the probe close to surface to save some measurement time, and press start.
4. The measurement will last as long as is indicated in the recipe (in default recipe it is 10 min) or until the stop button is pressed.

5.4 Measurements with platinum rod

A 1 mm in diameter platinum rod can be used for surface tension measurements. Use of the platinum rod enables surface tension measurements of small volumes. The measurement itself is performed as a standard Wilhelmy plate surface tension measurement.

Fill in the Recipe in the same way as described in the manual for performing standard Wilhelmy plate surface tension measurements, except now as the probe type choose the round rod. Click the empty field at the probe selection in the recipe, right click the window that appears and choose "Add". An "Editor" window will appear. When using the Pt Rod choose "Round Rod" as the Probe type and fill in the exact radius of the Pt Rod in the r field of the "Editor" window. The wetted length is then automatically calculated by the software.

Note! The exact diameter of the Pt Rod is given on the box holding the Pt Rod.

Hereafter, proceed as in a standard Wilhelmy Plate surface tension experiment.

5.5 Analysis of the surface and interfacial tension data

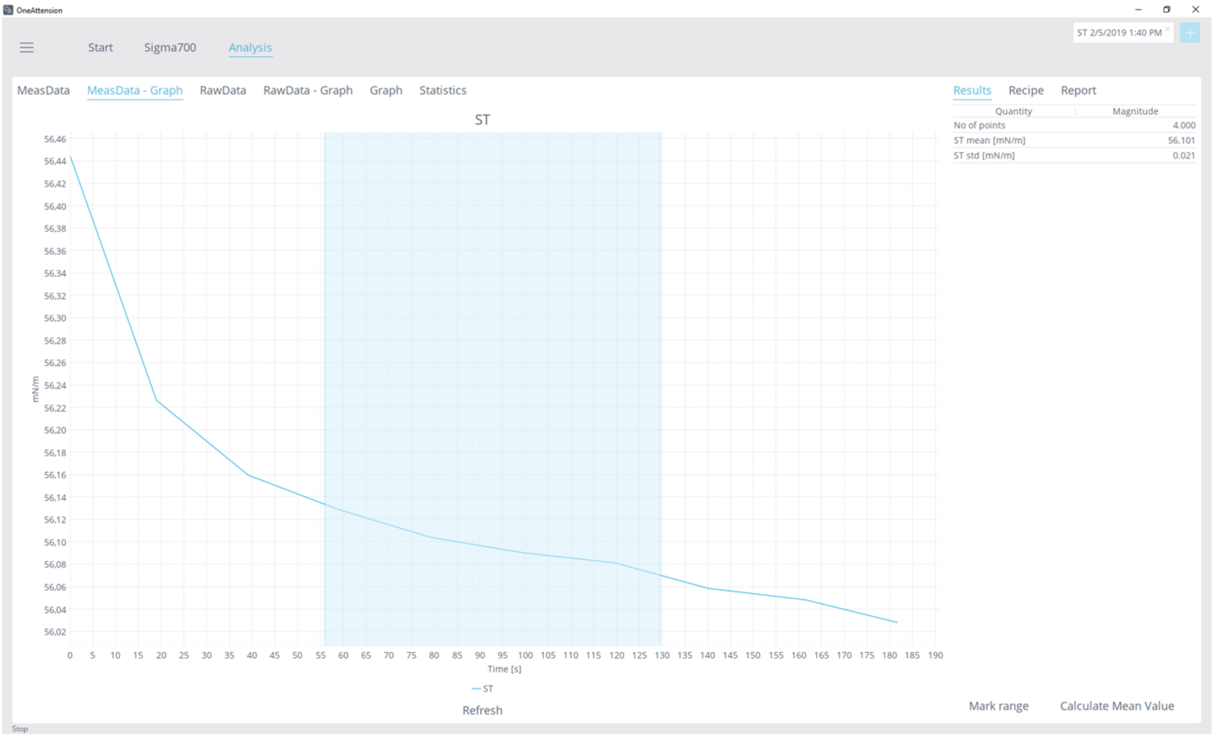
The measurements can be opened in the **Analysis tab** by double clicking the measurement you want to analyze.

Measured data and Measured graph are presented as well as raw data and raw data graph if selected to be saved in the recipe before the measurement was started. Now it is possible to calculate mean values and draw graphs as already explained in section 4.3.. It is also possible to change the dimensions of the probe or the density of the liquid in case of the Du Noüy ring measurements. The results are re-calculated automatically. This is very handy if the parameters inserted into recipe are later found to be incorrect.

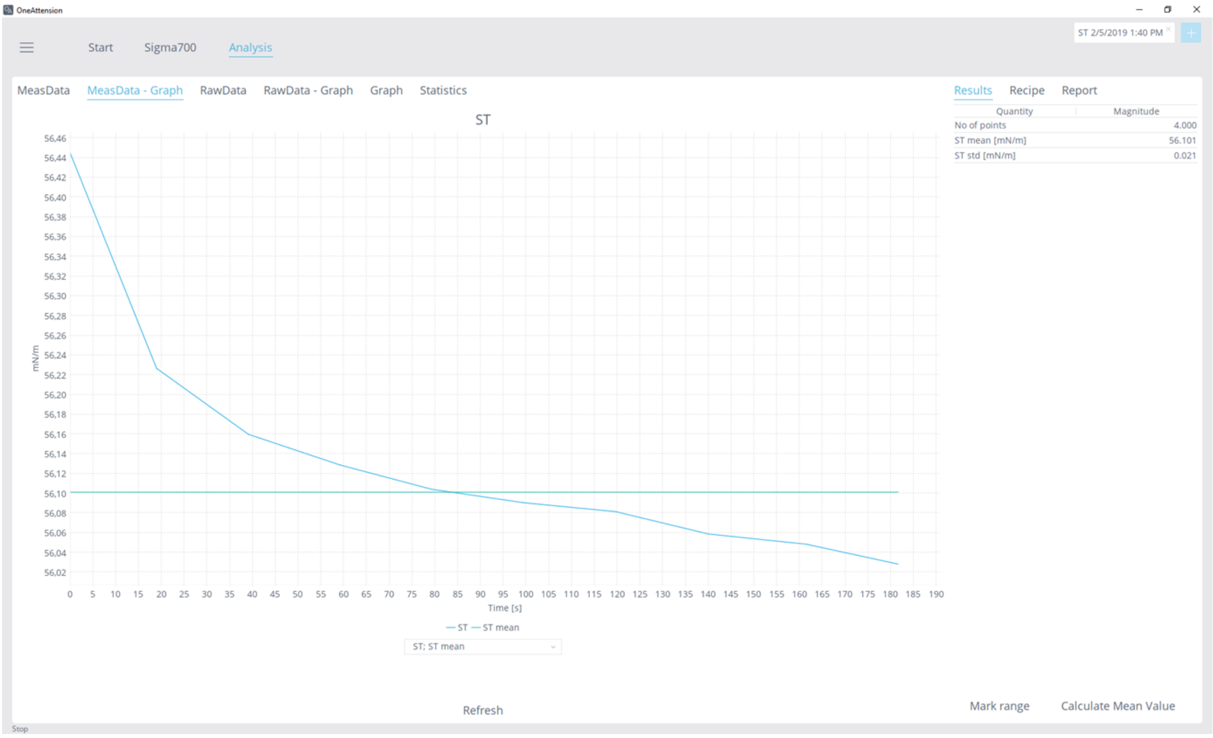
The buttons available for data analysis in the calculated results box are as follows:

Mark range: Enables the marking of the range in the graph for further calculations. Press this button and click the graph with your mouse first at point where you want to range to start and then click on the point where you want the range to end. The average surface tension will be calculated on this range.

Calculate Mean Value: When a range has been selected from the graph, the mean value in this range can be calculated by clicking this button.



Quantity	Magnitude
No of points	4.000
ST mean [mN/m]	56.101
ST std [mN/m]	0.021



Quantity	Magnitude
No of points	4.000
ST mean [mN/m]	56.101
ST std [mN/m]	0.021

5.6 Bath circulator controls

Bath circulator control parameters are visible on the Recipe sheet when a bath circulator is connected to the instrument. The following parameters are available:

Vessel target T (°C): Target temperature for the vessel

Use vessel as a target: If selected, temperature control loop is based on measured temperature of the vessel (Temperature probe in Sigma must be enabled at Global Settings). If not selected, temperature control loop is based on measured temperature of the bath circulator.

Bath max T (°C): Max. allowed temperature of bath liquid

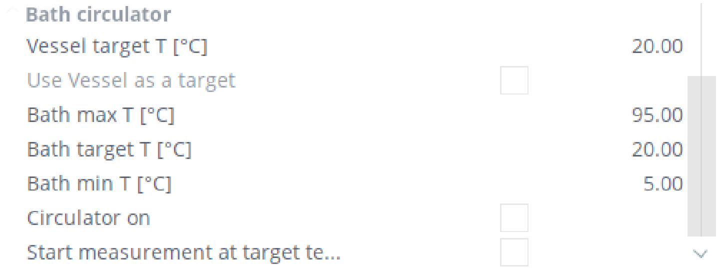
Bath target T (°C): Target temperature of bath liquid

Bath min T (°C): Min. allowed temperature of bath liquid

Circulator on: Select to start circulator operation. Deselect to stop operation.

Start measurement at target temperature: If selected, programmed experiment will start only when target temperature is reached. If not selected, the experiment will start immediately when Start button is pressed.

Also note that **Wait before start** under "Control Parameters" affects when the experiment starts. It can be used for example to allow more time for stabilization of target temperature after it has been reached.



Bath circulator
Vessel target T [°C] 20.00
Use Vessel as a target ☐
Bath max T [°C] 95.00
Bath target T [°C] 20.00
Bath min T [°C] 5.00
Circulator on ☐
Start measurement at target te... ☐

6 Dynamic contact angle measurement

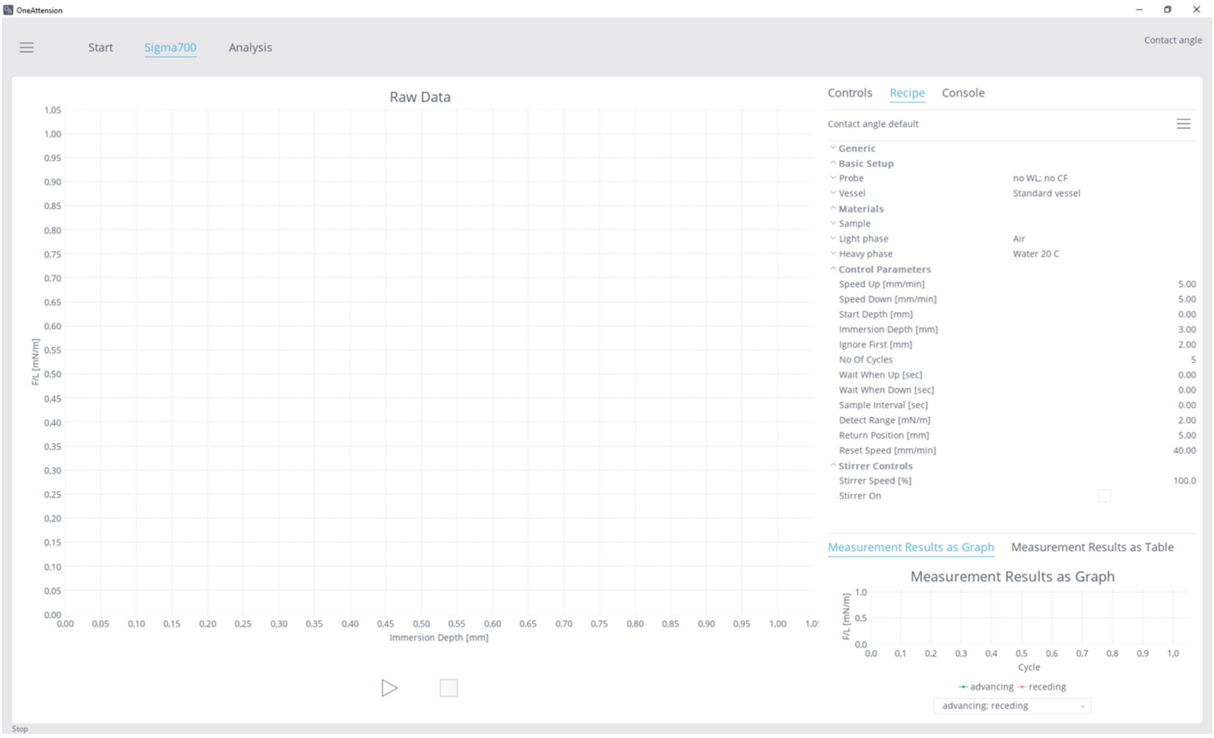
Dynamic contact angles can be measured by using Sigma 700/701. The measurement is based on the same Wilhelmy plate method as the surface tension measurement but this time the surface tension of the liquid has to be known and the contact angle is then calculated (See Theory chapter for further information). If you wish to use a known value for surface tension, simply enter it in the appropriate field in the recipe or select the liquid from the liquid database. You can also use the surface tension measurement to define the surface tension of your liquid in case it is not known.

The test solid can be any solid with a regular shape i.e. rectangular or square sheets, round or square rods, single fiber etc. The dimensions of the test solid have to be known. Note, that the test solid has to have the same properties all around i.e. the test solid has to be symmetrical and chemically the same overall. Test solids with different treatments on different sides cannot be used for standard dynamic contact angle measurements.

Many users may choose to run multiple cycles for contact angles. This approach can yield important data. The slope of F/L vs. Depth may be variable for a single direction and cycle. Multiple cycles can help to differentiate vibrational 'noise' from actual variability. Noise will be random, actual variability will be consistent for multiple cycles. Also the first cycle differs from subsequent cycles in that the probe is dry at the first immersion and wet thereafter. Probes that change upon wetting (either chemical change or absorption) will display differences in multiple cycles.

To proceed with the preparations of the measurement hang your test solid on the balance hook. Here, it is advisable to drive the stage meant for holding the liquid vessel to its lowest position by using the Manual Membrane Keyboard. Make sure your measuring vessel holding the liquid is thoroughly cleaned. Then place the vessel containing the liquid on the stage. Next choose the "Contact Angle" icon on the **Start tab**.

Your Contact Angle Measurement screen should appear as follows:



Contact angle default

Generic	
Basic Setup	
Probe	no WL; no CF
Vessel	Standard vessel
Materials	
Sample	
Light phase	Air
Heavy phase	Water 20 C
Control Parameters	
Speed Up [mm/min]	5.00
Speed Down [mm/min]	5.00
Start Depth [mm]	0.00
Immersion Depth [mm]	3.00
Ignore First [mm]	2.00
No Of Cycles	5
Wait When Up [sec]	0.00
Wait When Down [sec]	0.00
Sample Interval [sec]	0.00
Detect Range [mN/m]	2.00
Return Position [mm]	5.00
Reset Speed [mm/min]	40.00
Stirrer Controls	
Stirrer Speed [%]	100.0
Stirrer On	☐

The dynamic contact angle recipe contains the following fields (in addition to generic field):

Basic setup

Probe: Here the details of the sample are listed. The sample dimension can be selected from the database or the dimensions can be given manually. WL stands for "wetted length" and CF for "correction file".

Name: Name of the probe e.g. Sample 1

Type: Type of the sample can be selected from the list and can be either rectangular plate or round rod (for fibers)

R (or plate width) [mm]: Width of the Wilhelmy plate or radius of the fiber.

r (or plate thickness) [mm]: Thickness of the Wilhelmy plate. Not used in case of fibers.

Correction file: Correction file is not used in dynamic contact angle measurement.

Vessel: Details of the used vessel are listed here (not mandatory information for dynamic contact angle measurement). Vessel can be chosen from the database or given manually.

Name: Name of the vessel, e.g. Standard vessel.

Diameter [mm]: The diameter of the vessel.

Volume [ml]: The volume of the vessel.

Materials

Light Phase: The information about the light phase is listed here in details. The light phase can be chosen from the list or the information can be written. In case of dynamic contact angle measurement, the light phase is air, but this information is not used in calculation.

Name: Name of the light phase, e.g. air.

γ^{tot}: Total surface tension.

γ^{d}: Dispersive component of the surface tension.

γ^{+}: Base component of the surface tension.

γ^{-}: Acid component of the surface tension

ρ: Density

η: Viscosity

Temperature [°C]: Temperature at which the parameters are defined.

Molecular weight [g/mol]: Molecular weight

Heavy Phase: The information about the heavy phase is listed here in details. In case of dynamic contact angle measurements, the heavy phase is the liquid that is used for measurement. Heavy phase can be selected from the database or it can be given manually. The surface tension of the heavy phase is required.

Control Parameters

Speed Up [mm/min]: Speed at which probe moves during withdrawal

Speed Down [mm/min]: Speed at which probe moves during immersion

Start depth [mm]: Where the sample is lift after the measurement

Immersion depth [mm]: The depth to which the sample is immersed.

Ignore first [mm]: The first x mm of the sample after immersion is not used for the contact angle measurement.

No of Cycles: How many contact angle measurement cycles are performed.

Wait when up [sec]: Waiting time after each measurement cycle.

Wait when down [sec]: Waiting time when the sample is at the lowest immersion depth.

Sample interval [sec]: How often the measurement data point is collected. Zero means as fast as possible (limited by the speed of the balance).

Detect range: Amount of change in force, which will register as contact with interface. If the liquid interface is detected before the actual contact of the probe has taken place, this value is set too low. If the surface is not detected, this value is set too high.

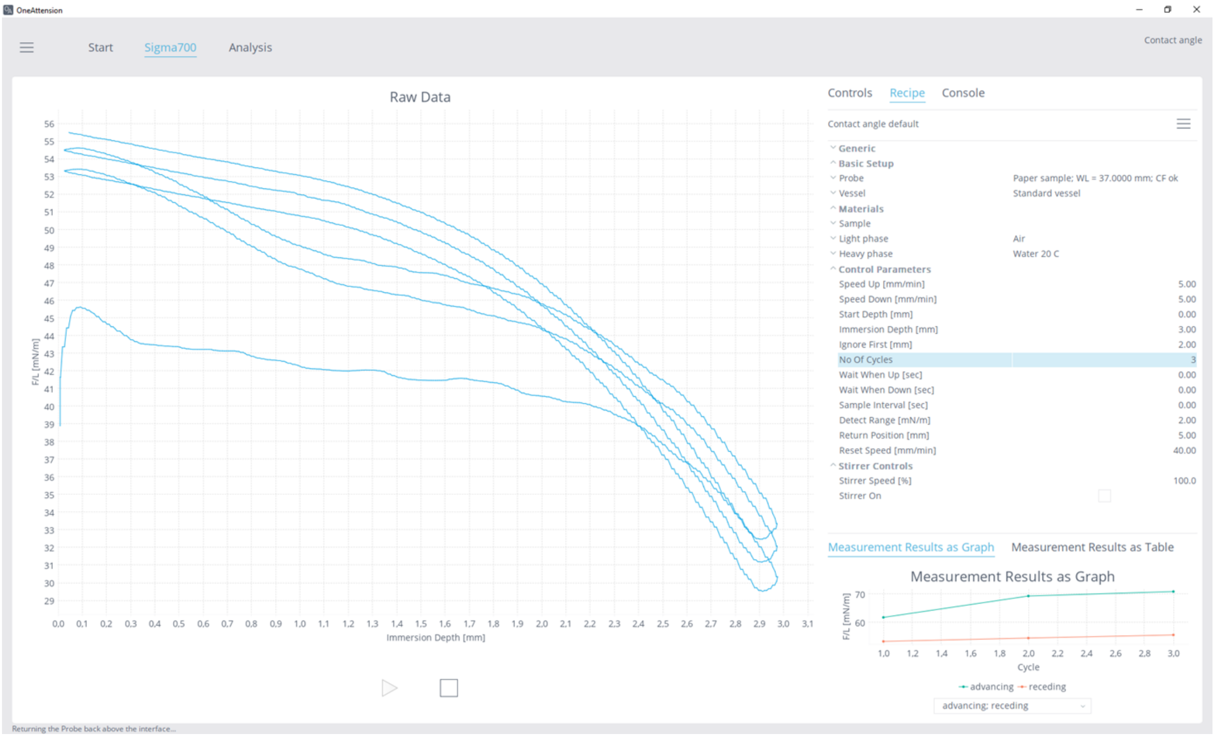
Return position: Position above interface to which the probe will return in between the measurements.

Reset speed: The speed of the probe when not doing an experiment but controlling the probe manually.

6.1 Step by step instructions for a dynamic contact angle measurement

1. Hang the sample on the hook by using a suitable probe.
2. Fill at least the following fields in the default recipe or load a previously saved recipe:
    - Experiment name
    - Sample dimensions, the width and the thickness of the sample are needed to define the perimeter of the sample. The length of the sample is not important since that is defined by the immersion depth. When measuring single fibers, choose rod as a probe and insert the radius of the fiber into the recipe
    - Select the suitable heavy phase or at least insert the surface tension value for the heavy phase.
3. Fill the beaker with the heavy phase.
4. Bring the probe close to surface to save some measurement time, and press start.
5. The Contact Angle Measurement window will during the experiment show in real time the Force/Wetted length vs. time graph. Measured values are listed in the "Measurement Results as Table" tab of the contact angle measurement window (see figure below).
6. The device will make as many measurements as indicated in the recipe (No of cycles) and stop after that or when the stop button is pressed.

NOTE! It is very important to define the shape and perimeter of the test solid in the Experimental Setup for a successful outcome of your measurement. The perimeter is the length of the solid substrate that is in contact with the liquid during immersion/withdrawal i.e. for a rectangular plate the perimeter = (2 × width of plate + 2 × thickness of plate), for a round rod the perimeter = (2 × π × radius of rod) etc.



Contact angle default

Generic	
Basic Setup	
Probe	Paper sample; WL = 37.0000 mm; CF ok
Vessel	Standard vessel
Materials	
Sample	
Light phase	Air
Heavy phase	Water 20 C
Control Parameters	
Speed Up [mm/min]	5.00
Speed Down [mm/min]	5.00
Start Depth [mm]	0.00
Immersion Depth [mm]	3.00
Ignore First [mm]	2.00
No Of Cycles	3
Wait When Up [sec]	0.00
Wait When Down [sec]	0.00
Sample Interval [sec]	0.00
Detect Range [mN/m]	2.00
Return Position [mm]	5.00
Reset Speed [mm/min]	40.00
Stirrer Controls	
Stirrer Speed [%]	100.0
Stirrer On	☐

Returning the Probe back above the interface...

6.2 Practical tips for contact angle measurement of fibers

Fibers of a variety of sizes are easily tested for contact angles. It is not unreasonable to expect that you can get good results for fibers with diameters below 10µm. This however may require the use of cabinet to protect the instrument from air flow and anti-vibration table. The accuracy of your results is directly related to the accuracy of your measurement of the perimeter of the fiber. For larger, more rigid fibers the technique is straightforward and requires no additional comment. For fibers, which are smaller and less rigid, the following comments merit your attention.

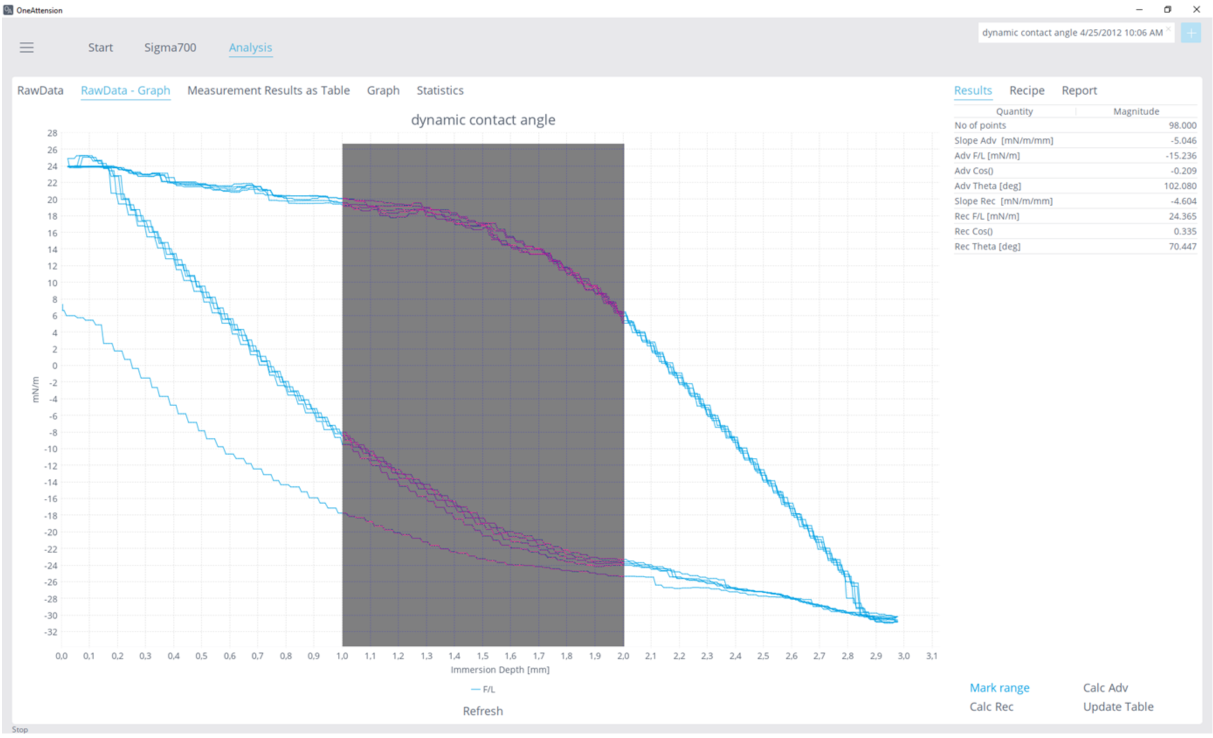
Attension makes sample holders, which make fiber mounting simple.

The fiber sample needs to be able to penetrate the surface of your liquid and maintain a vertical orientation as it moves through the liquid. For this reason, you may have to trim very small and limp fibers to less than 5mm length. Although it is useful to assay longer lengths of the sample, lengths as short as 2 mm can yield good data. If your fiber is not rigid and/or wets poorly with your liquid, you will notice that it resists penetration of the surface. In such a case you should attempt to shorten the length of the sample until you achieve penetration.

The smaller the fiber sample size is, the more system noise there is in relation to the signal (e.g. signal-to-noise ratio decreases as fiber sample size decreases). It might be useful to increase detect range in order to avoid false liquid interface detections (i.e. detections of the liquid interface before actual contact with the interface occurs). It is helpful to monitor the real time balance output for a while and set detect range to a value that is higher than the range where the balance output fluctuates.

6.3 Analysis of the dynamic contact angle data

The measurements can be opened on the **Analysis tab** by double clicking the measurement you want to analyze. Raw data, raw data-graph and measurement results as table are presented. It is quite common that the first advancing angle is different than the subsequent ones since before the first dipping the sample is dry whereas after that it is already wetted. You can calculate the average advancing and receding contact angles from the table by selecting the contact angle values you want to use for the calculations and pressing the right button of the mouse and statistics. It is also possible to select the area from the graph. That way it is possible to choose a certain length for the calculations, for example, in the figure above area from 1 cm to 2 cm is selected. Note that the contact angles will be averaged over this whole area, so both sides of the sample have to be the same.

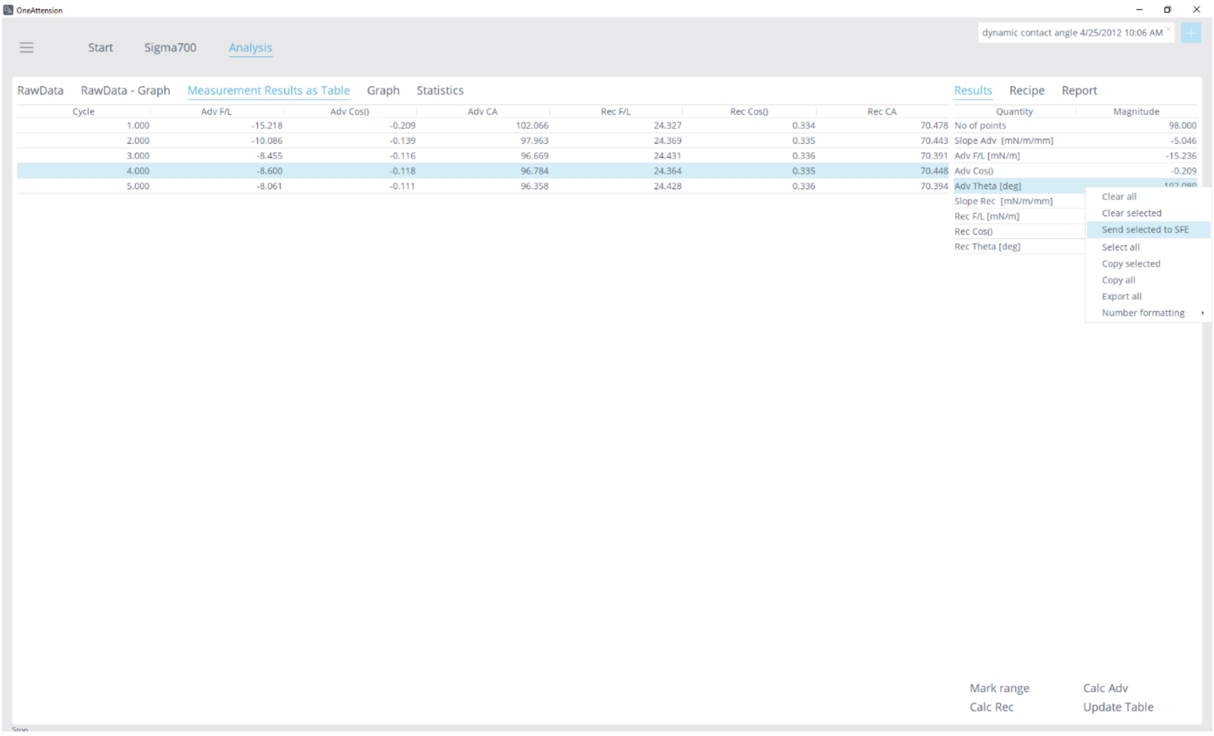


Quantity	Magnitude
No of points	98.000
Slope Adv [mN/m/mm]	-5.046
Adv F/L [mN/m]	-15.236
Adv Cos()	-0.209
Adv Theta [deg]	102.080
Slope Rec [mN/m/mm]	-4.604
Rec F/L [mN/m]	24.365
Rec Cos()	0.335
Rec Theta [deg]	70.447

You can also edit the recipe. This can be very helpful if you wish to recalculate the data produced based on new information about the materials involved. For example, if you performed a contact angle experiment and estimated the perimeter of your probe to be 10 mm and later found that the actual perimeter was 11 mm you could enter this new information into the recipe. Press Update table and the corrected contact angle values will appear in the table.

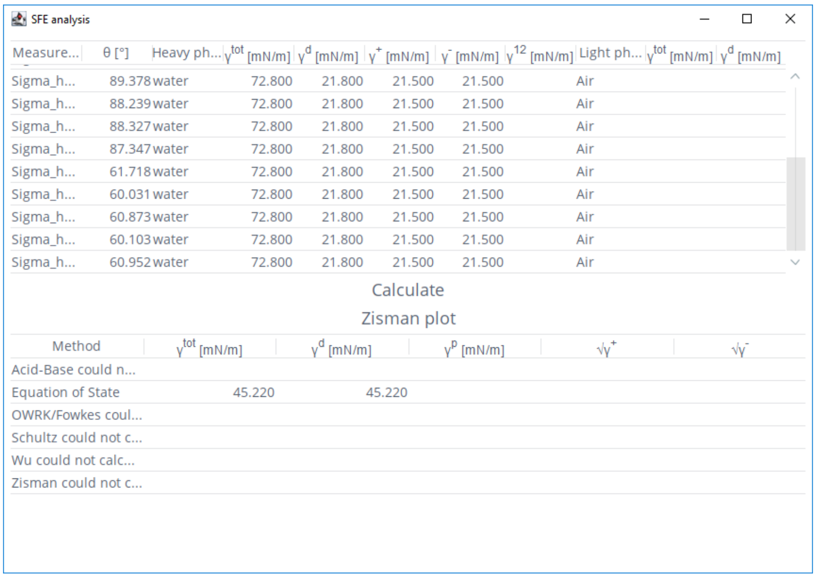
6.3.1 Surface free energy calculations

It is also possible to calculate the surface free energy (SFE) of the solids by using Sigma and OneAttension. Quite often the advancing contact angle is then utilized. The use of SFE calculator is simple. Just calculate the average contact angle so that it appears on the results tab. Highlight the contact angle value on that window and press the right button of the mouse. Press "send selected to SFE". After that the SFE Window will open. You can do the same to other contact angle measurement done with the same sample. Note that you should not close the SFE window but keep it open in the background when sending contact angle results to SFE calculator. After sending all the results, press calculate and the surface free energy is calculated based on the most used SFE theories. You should perform the contact angle measurements with at least two different liquids for OWRK and Wu methods and with at least three liquids for Acid-Base method. You can also perform multiple measurements with the same liquid. The SFE calculator will first calculate the average contact angle for that liquid and then the actual SFE values.



Cycle	Adv F/L	Adv Cos()	Adv CA	Rec F/L	Rec Cos()	Rec CA
1.000	-15.218	-0.209	102.066	24.327	0.334	70.478
2.000	-10.086	-0.139	97.963	24.369	0.335	70.443
3.000	-8.455	-0.116	96.669	24.431	0.336	70.391
4.000	-8.600	-0.118	96.784	24.364	0.335	70.448
5.000	-8.061	-0.111	96.358	24.428	0.336	70.394

Quantity	Magnitude
No of points	98.000
Slope Adv [mN/m/mm]	-5.046
Adv F/L [mN/m]	-15.236
Adv Cos()	-0.209
Adv Theta [deg]	102.080
Slope Rec [mN/m/mm]	
Rec F/L [mN/m]	
Rec Cos()	
Rec Theta [deg]	



Measure...	θ [°]	Heavy ph...	γ^{tot} [mN/m]	γ^{d} [mN/m]	γ^{+} [mN/m]	γ^{-} [mN/m]	γ^{12} [mN/m]	Light ph...	γ^{tot} [mN/m]	γ^{d} [mN/m]
Sigma_h...	89.378	water	72.800	21.800	21.500	21.500		Air		
Sigma_h...	88.239	water	72.800	21.800	21.500	21.500		Air		
Sigma_h...	88.327	water	72.800	21.800	21.500	21.500		Air		
Sigma_h...	87.347	water	72.800	21.800	21.500	21.500		Air		
Sigma_h...	61.718	water	72.800	21.800	21.500	21.500		Air		
Sigma_h...	60.031	water	72.800	21.800	21.500	21.500		Air		
Sigma_h...	60.873	water	72.800	21.800	21.500	21.500		Air		
Sigma_h...	60.103	water	72.800	21.800	21.500	21.500		Air		
Sigma_h...	60.952	water	72.800	21.800	21.500	21.500		Air		

Method	γ^{tot} [mN/m]	γ^{d} [mN/m]	γ^{p} [mN/m]	$\sqrt{\gamma^{+}}$	$\sqrt{\gamma^{-}}$
Acid-Base could n...					
Equation of State	45.220	45.220			
OWRK/Fowkes coul...					
Schultz could not c...					
Wu could not calc...					
Zisman could not c...					

7 Critical micelle concentration measurement

To perform automated critical micelle concentration measurements, one or two TITRONIC® 300 dispensers are required.

In the case of one dispenser, the measurement is started with pure water in the vessel and the dispenser adds surfactant solution to the beaker. In the case of two dispensers, the measurement is started with surfactant solution in the beaker. First dispenser is then adding pure water into the vessel while the other dispenser removes surfactant solution from the vessel. The surfactant solution is diluted over the CMC point.

7.1 Setting up the dispenser(s)

The following steps are needed to set up the dispenser (or dispensers) prior to performing an experiment:

1. Physical setup, including connecting tubes
2. Configuring the filling dispenser
3. Configuring the removing dispenser (if used)
4. Configuring PC and OneAttension

7.1.1 Physical setup of the dispenser(s)

If only one dispenser is used, it's the filling dispenser. If two dispensers are used, the first dispenser if the filling one and the second is the removing one.

1) Remove the rubber hole covers on Sigma to make room for all the tubes and cables to go through the holes.

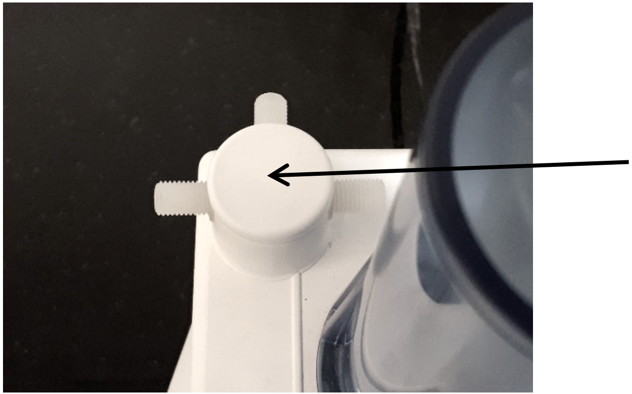
Remove rubber covers (2) from the back wall of Sigma

2) CMC measurements typically require the use of a magnetic stirrer. The magnetic stirrer comes preinstalled under the sample stage. Plug in the stirrer to the side panel of the Sigma.

Attach the magnetic stirrer. In case you will be using the temperature probe, attach it similarly as well to the middle port.

3) In case temperature probe is also used during the measurement, connect it also to the side of the Sigma so that the probe is inside the Sigma measuring chamber.

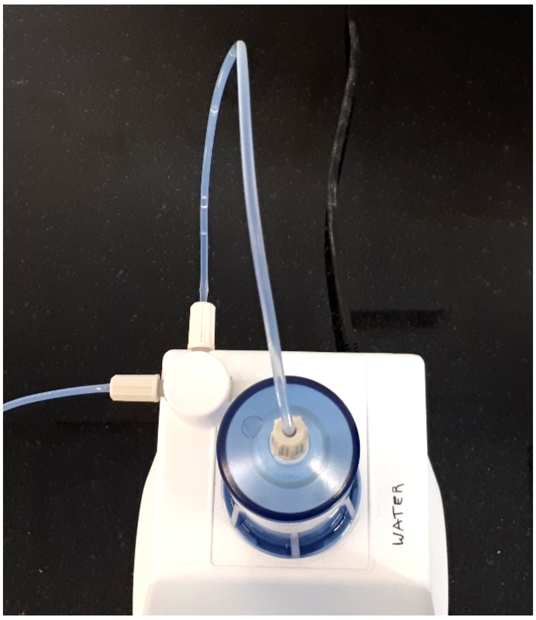
4) Set the filling dispenser on the table on the left side of the Sigma. Plug it into the mains.
5) Place the tube from the left side of the Titronic adapter (when viewed from the top as in below image) into the bottle delivered with the instrument. Fill the bottle with surfactant solution of known concentration (if one-dispenser setup) or with DI-grade water (if two-dispenser setup). Make sure the end of the tube is firmly in the liquid.



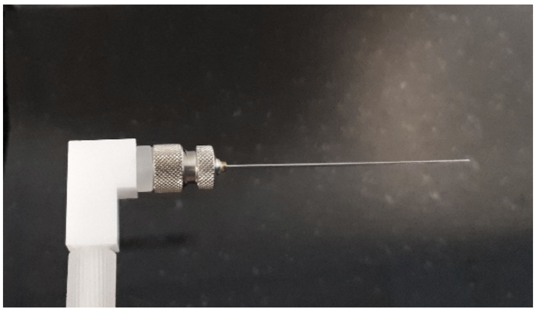
Titronic tube adapter from top view. Left side is for filling the Titronic, middle for the Titronic piston and right for dispensing. In the filling Titronic, the left side goes to the bottle with the filling liquid inside.

Tubing from the left side of the dispenser into the filling bottle.

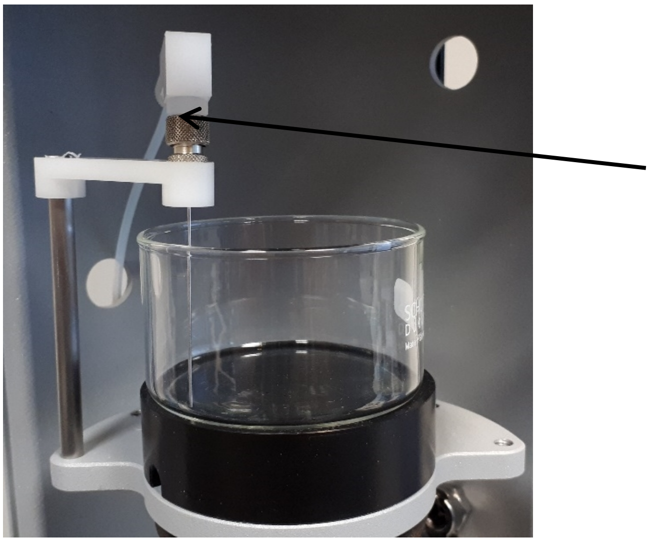
6) Make sure the tubing from the Titronic piston is attached to the middle of the Titronic tube adapter.



7) Place the tube from the right side of the Titronic adapter through the hole on the Sigma frame. Connect the needle to this end by fixing the threads. Use only moderate force as excess force may damage the threads.



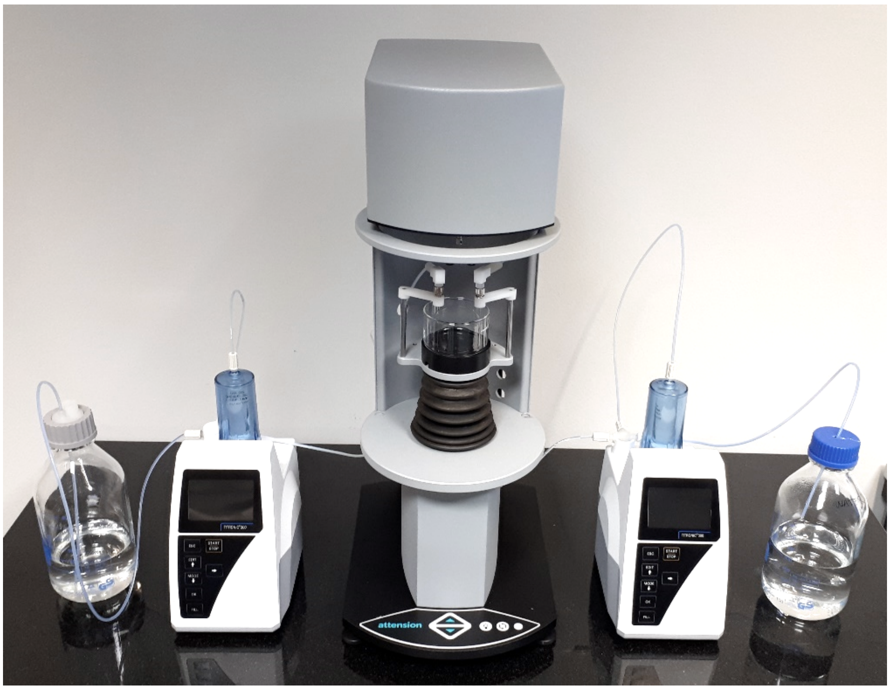
8) Place an empty glass vessel onto the Sigma sample stage. Attach the needle fixing pole and adapter to the sample stage. Insert the needle through the hole so that the needle end is in the empty vessel.



Tube from the right side of the Titronic tube adapter goes inside the Sigma. Needle attaches to the tubing. Needle placed in the glass vessel in its holder.

9) The complete setup with one dispenser is illustrated in below image.

10) If you are using two dispensers, set the removing dispenser on the table on the right side of the Sigma. Plug it into the mains
11) With the removing (right) dispenser the tubes are connected differently than with the filling (left) one.
12) Place the tube from the left side of the Titronic adapter inside the Sigma through the hole in the Sigma frame. Connect the needle to this end by fixing the threads. Use only moderate force as excess force may damage the threads.
13) Attach the needle fixing pole and adapter to the sample stage. Insert the needle through the hole so that the needle end is in the empty vessel.
14) Make sure the tubing from the Titronic piston is attached to the middle of the Titronic tube adapter.
15) Place the tube from the right side of the Titronic adapter into another bottle delivered with the instrument. This is the waste bottle in this measurement.
16) The complete setup with two dispensers is illustrated in below image.



17) Please notice that the Titronic boxes also include a multitude of accessories only needed for titration, not CMC. Those parts such as mouse and different holders are not required in CMC installation.

7.1.2 Configuring the filling dispenser

18) Turn on the filling dispenser on the left without connecting it to your PC.
19) Change the language of dispenser if needed
    a. Press **mode** button
    b. Select System settings
    c. Select Language settings
    d. Select language
20) Change the dispensing rate of the adding dispenser (if the dispensing rate is too high there can be some leakage at the connection of the tubing and needle).
    a. Press **edit** button
    b. Select Edit method
    c. Select Dosing parameter
    d. Select Dosing speed
    e. Change the speed to 5 ml/min
21) Make sure the bottle contains liquid and the end of the tube is firmly in the liquid.
22) On the left Titronic dispenser, press Start and dispense 70 ml. The Titronic will now fill up its piston and run some liquid through the system. After the Titronic is done, check that there are no air bubbles inside any of the tubes. If there are, dispense more liquid out until there is no air left. Once all the air has been removed, finally select Fill on the Titronic to fill it up. The dispenser is now physically set up for the measurement.
23) Change the connection type to USB on the dispenser
    a. Press **mode** button
    b. Select System settings
    c. Select RS232 Settings
    d. Select RS232-1 Settings
    e. Select Connection
    f. Change the connection to USB
    g. Turn off the dispenser

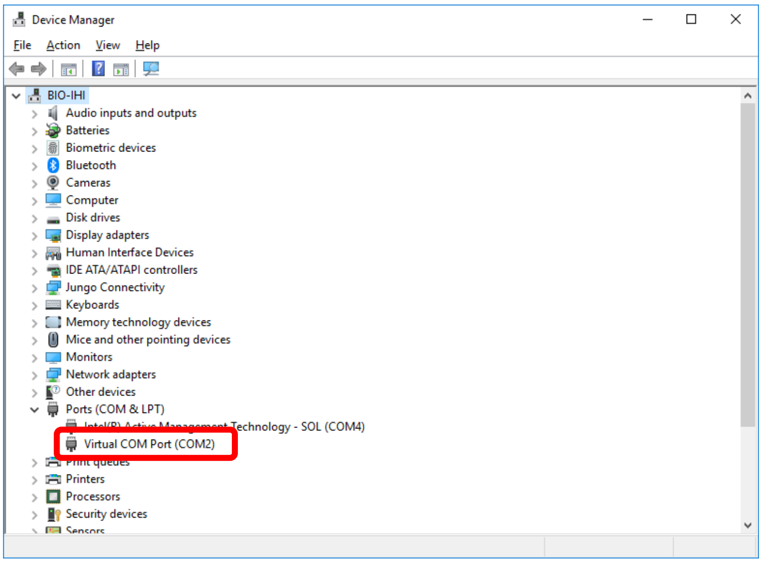
7.1.3 Configuring the removing dispenser (if used)

24) In case two dispensers are used, turn on the removing dispenser on the right without connecting it to your PC.
25) Change the language of dispenser if needed
    e. Press **mode** button
    f. Select System settings
    g. Select Language settings
    h. Select language
26) Change the filling time of the dispenser
    a. Press **edit** button
    b. Select Filling speed
    c. Change filling time to at least 120 s (if there are still some air bubbles sucked in, increase the filling time even more).
27) Change the connection type to USB on the dispenser
    a. Press **mode** button
    b. Select System settings
    c. Select RS232 Settings
    d. Select RS232-1 Settings
    e. Select Connection
    f. Change the connection to USB

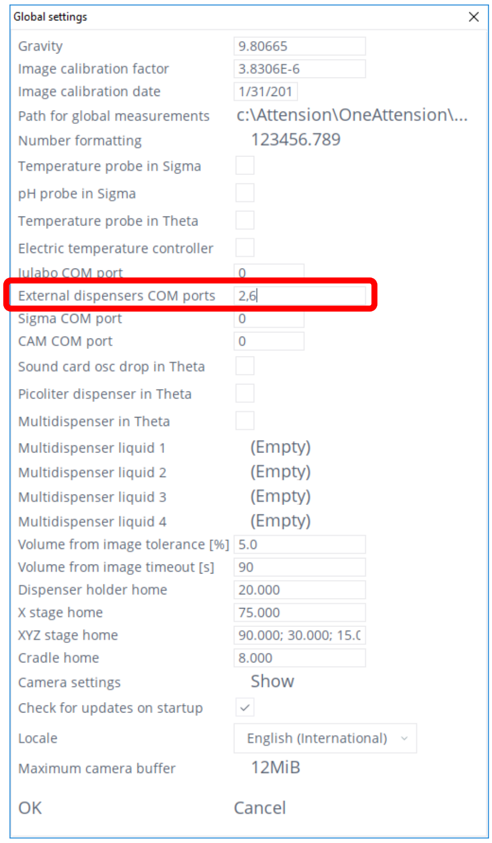
g. Turn off the dispenser

7.1.4 Configuring PC and OneAttension

28) Install Virtual COM port (VCP) drivers on your computer.
    a. Turn on the left dispenser and connect to the PC via USB.
    b. Then turn on the right dispenser (if used) and connect it to the PC via USB.
    c. On your OneAttension installation USB drive, go to Drivers → Titronic 300 folder. Run dpinst.exe (if you have a 32-bit version of Windows) or dpinst_x64.exe (if you have a 64-bit version of Windows).
    d. Choose “Yes”, “Next” or “Install” on all the questions asked by the installer.
    e. The driver is now installed on your PC.
29) Open Windows Device Manager. The dispenser(s) will be visible as a Virtual COM port under Ports (COM & LPT). Check the COM port number(s).



30) Turn off the dispenser(s).
31) Turn on first the Sigma, then the left dispenser, followed by the right dispenser and finally OneAttension software.
32) In OneAttension, open main menu → Global settings. Check that the Virtual COM Port numbers (that was checked above) are listed on the External dispensers COM ports field. If not, add them there and remember to click OK.
    a. However, very high COM port numbers (> 9) do not usually work. Then it is advised to change the number of the COM port from the Device Manager. Select the COM port you want to modify. Right click and select properties. From port settings open advanced and select the COM port number from the list.
    b. If you are using two dispensers, use the device with the lower COM port number as the left dispenser and the dispenser with the higher COM port number as the right dispenser. Make sure they are listed in External dispensers COM ports field so that the smaller COM port number is put in first, and the larger second (e.g. 2,6).



Gravity: 9.80665
Image calibration factor: 3.8306E-6
Image calibration date: 1/31/201
Path for global measurements: c:\Attension\OneAttension\...
Number formatting: 123456.789
Temperature probe in Sigma: ☐
pH probe in Sigma: ☐
Temperature probe in Theta: ☐
Electric temperature controller: ☐
Julabo COM port: 0
External dispensers COM ports: 2,6
Sigma COM port: 0
CAM COM port: 0
Sound card osc drop in Theta: ☐
Picoliter dispenser in Theta: ☐
Multidispenser in Theta: ☐
Multidispenser liquid 1: (Empty)
Multidispenser liquid 2: (Empty)
Multidispenser liquid 3: (Empty)
Multidispenser liquid 4: (Empty)
Volume from image tolerance [%]: 5.0
Volume from image timeout [s]: 90
Dispenser holder home: 20.000
X stage home: 75.000
XYZ stage home: 90.000; 30.000; 15.0
Cradle home: 8.000
Camera settings: Show
Check for updates on startup: ☑
Locale: English (International)
Maximum camera buffer: 12MiB

33) The sigma and the dispenser(s) are now ready to be used.

7.2 Experiment

When the dispensers are connected and the CMC measurement is opened, the following window will open.

CMC plate default
Generic
Basic Setup
Probe: Wilhelmy plate; WL = 39.2400 m...
Vessel: Standard vessel
Materials
Light phase: Air
Heavy phase: Water 20 C
Volume [ml]
Addition
Cmc Parameters
Start Conc: 0.00E0
End Conc: 0.00E0
Points/Decade: 5
Max Deviation [mN/m]: 2.0
Max Meas Time [min]: 10.0
AutoSearch: ☐
AutoPoints/Decade: 2
Pressure Drop [mN/m]: 2.0
Stir after Adding [sec]: 10.0
Wait after Stir [sec]: 5.0
Stirrer Speed [%]: 100.0
Use two Dispensers: ☐
Wilhelmy Parameters
Speed Up [mm/min]: 20.00

CMC measurements can be performed either by using Du Noüy ring or Wilhelmy plate. The selection should be made when the measurement is opened.

The critical micelle concentration recipe contains the following parameters (in addition to generic fields):

Basic setup

Probe: Here the details of the selected probe are listed. The probe can be selected from the database or the dimensions can be given manually. WL stands for "wetted length" and CF for "correction file". Please see more information about the probe setting under surface tension measurements with Du Noüy ring or Wilhelmy plate.

Vessel: Details of the used vessel are listed here. Information of the vessel volume is especially important when only one dispenser is used. This is because the information is used to calculate the maximum amount of liquid that can be added into the vessel. If the volume of the vessel is larger in the recipe, there is a risk of overflow. When two dispensers are used, this is not as critical. Vessel can be chosen from the database or given manually.

Name: Name of the vessel, e.g. Standard vessel.

Diameter [mm]: The diameter of the vessel.

Volume [ml]: The volume of the vessel.

Analysis baseline tilt: Chosen when tilt is allowed in fitting of the baseline. When not chosen, the baseline will be a horizontal line.

Materials

Light Phase: The information about the light phase is listed here in details. The light phase can be chosen from the list or the information can be written. In case of CMC measurements, the light phase is air. The density of the light phase is required when Du Noüy ring is used.

Name: Name of the light phase, e.g. air.

γ^{tot}: Total surface tension.

γ^{d}: Dispersive component of the surface tension.

γ^{+}: Base component of the surface tension.

γ^{-}: Acid component of the surface tension

ρ: Density

η: Viscosity

Temperature [°C]: Temperature at which the parameters are defined.

Molecular weight [g/mol]: Molecular weight

Heavy Phase: The information about the heavy phase is listed here in details. In case of CMC measurements, the heavy phase is the liquid that is measured. Density is required when Du Noüy ring is used. Since most often surfactant solutions are measured, the density can be assumed to be that of water.

Volume [ml]: The volume of the solution in the vessel. In case of one dispenser the solution is usually pure water. In case of two dispensers, the solution is concentrated surfactant solution.

Addition: This contains additional information about the solutions used in the measurement

Name: The name of the surfactant solution (one dispenser) or water (two dispensers).

Concentration: Concentration of the surfactant solution (one dispenser) and zero (two dispensers, since only water is added).

Initial concentration: Initial concentration in the vessel. Usually zero (one dispenser, since there is water), concentration of the surfactant solution (two dispensers).

Unit: The unit of concentration

CMC parameters

Start Conc: Concentration in vessel after first addition (one dispenser) or concentration in the vessel at the beginning, same as initial concentration in the recipe (two dispensers). This is calculated by the software after the start button is pressed for the first time. It can be changed to bigger value when one dispenser is in use or smaller value when two dispensers are used.

End Conc: Concentration in vessel at end of run. When one dispenser is used the end concentration is calculated by taking the total volume of the dispenser into account. It can be changed to smaller value. When two dispensers are used, this is a very low concentration that can be changed to bigger value.

Points/Decade: Number of concentrations (per decade of log scale) assayed. Additions will be set for even spacing on log scale.

Max Deviation [mN/m]: Maximum deviation in between two consecutive surface tension measurements which will be accepted as indication of stability. If the deviation of the surface tension value is bigger than that, another surface tension measurement will be conducted at same concentration.

Max Meas Time [min]: Maximum time surface tension measurement will occur at single concentration if Max Deviation stability not achieved

AutoSearch: When selected the software uses lower number of points per decade until the drop in surface tension is detected. If the CMC is completely unknown, this function can make it faster to find the correct range for the CMC.

AutoPoints/decade: How many points per decade are used during Autosearch.

Pressure Drop: Decrease in surface tension, which will trigger switch to standard points per decade mode.

Stir after adding: Time for which stirrer will be active after addition.

Wait after Stir: Delay after stirring before measurement.

Stirrer speed [%]: The percentage from maximum stirrer speed. 100 % is the full speed.

Use two dispensers: Chosen when experiment is done with two dispensers.

Ring parameters

Speed Up: Speed at which probe moves during withdrawal

Speed Down: Speed at which probe moves during immersion

Dwell Down 1 [%]: Amount of drop in F/L (in % from maximum measure value) between each measurement cycle or pull. When the surface tension is really low, it might be useful to increase this value.

Dwell Down 2 [%]: Amount of drop in F/L (in % from maximum measure value) between each concentration. Usually set to 100 %.

Wait between: Wait time in between the measurements

Detect range: Amount of change in force, which will register as contact with interface. If the liquid interface is detected before the actual contact of the probe has taken place, this value is set too low. If the surface is not detected, this value is set too high.

Start depth: The depth from where the experiment is started.

Go below start: Probe is immersed lower than the starting position.

Return position: The position where the probe is returned to after the experiment.

Reset speed: The speed of the probe when not doing an experiment but controlling the probe manually.

Automatic surface detection: When selected the balance is automatically zeroed when empty and the position is zeroed at the surface.

Push Mode: When Push mode is selected, the ring is pushed down in the heavy phase. When Push Mode is selected, Automatic surface detection is always unselected.

Wilhelmy parameters

Speed Up: Speed at which probe moves during withdrawal

Speed Down: Speed at which probe moves during immersion

Wetting depth: The depth to which the plate is immersed. This is calculated as part of the Wetted length.

Wait between: Wait time in between the measurements

Stabilize [sec]: Time to wait before starting to collect data.

Integrate [sec]: Time during which the data is collected (results is an average over this time period). This will reduce noise since not only one measurement point is taken as a result but several are averaged over selected time.

Detect range: Amount of change in force, which will register as contact with interface. If the liquid interface is detected before the actual contact of the probe has taken place, this value is set too low. If the surface is not detected, this value is set too high.

Start position: Position above interface to which the probe will return in between the measurements.

Reset speed: The speed of the probe when not doing an experiment but controlling the probe manually.

Zero When Wet: Zero the balance after wetting the probe

Wet First Only: When active, the probe is wetted only once before the measurements. When inactive, the probe is wetted before each individual surface tension measurement.

7.2.1 Using one TITRONIC® 300 dispenser

1. Turn on the CMC measurement by clicking the icon. The software will ask whether you want to measure with the ring or with the plate. Either of them can be selected.

2. Put the surfactant solution into a bottle. **Note! Before you start the measurements, all the tubes of the Titronic have to be filled with the surfactant solution.**
    a. Fill the piston manually by pressing **fill** button on the dispenser. After the filling is done, Titronic will stop automatically.

   b. Let some surfactant solution out from the needle by pressing the **start/stop** button on the dispenser (put a cup under the needle). Dispense the surfactant solution as long as you can see air bubbles in the tubes. You can stop dispensing by pressing the **start/stop** button again.
   c. Fill the piston one more time by pressing **fill** button on the dispenser.

3. Put a known volume of pure water to clean beaker. At least 30 ml is recommended.

4. Fill in the recipe
   a. Experiment name
   b. Check that the dimensions of the probe are correct
   c. Select the suitable vessel (Note that the dimensions have to be correct for the program to know when the vessel is filled)
   d. Select the suitable light phase (in case of CMC it is air) and heavy phase (water)
   e. Insert the volume of the heavy phase (= the volume of water in the beaker). Use at least 30 ml of liquid.
   f. Fill in the addition fields; concentration is the concentration of your surfactant solution in the large bottle. Concentration should be about one order of magnitude higher than expected CMC point. Initial concentration is the surfactant concentration in the beaker and is zero since there is pure water. Select the unit (depends on which unit you have used as concentration of surfactant solution, typically mol/l).
   g. You may want to change the stir after adding and wait after stirring times to be longer (e.g. 60 s) to ensure even distribution of surfactant molecules and stable surface.
   To calculate how much surfactant is needed for certain concentration, the equation

$$m = M * V * c$$

   can be used, where m is the mass of the surfactant, M is the molar mass of the surfactant, V is the total volume (usually it is good idea to make at least half a liter of solution) and c is the concentration. Notice that the concentration has to be well above the CMC concentration of the surfactant.

5. Attach the ring/plate to a hook. Put the beaker in its place and magnetic rod in the beaker (if stirrer is used). Put the needle in the beaker as well as temperature probe (if used). Bring the ring/plate close to the surface.
6. Press start.
7. The software will now tell you that you can change the start concentration to be higher and the end concentration to be lower. The default start concentration is concentration after first addition (0.01 ml) and the default end concentration the concentration when the beaker is full. These are calculated automatically by the software but can be changed if needed. If not press start again.
8. The device will first measure the initial surface tension of the water, then add some surfactant while stirring at the same time and measure the surface tension of the solution at that concentration. This will continue until the end concentration is achieved or the beaker is full.
9. If the beaker is full before the CMC point is reached, you have to manually empty the known amount of solution from the beaker. Then you have to start a new experiment. Remember to change the initial concentration! The results from two separate measurements can be combined in Excel for example.

7.2.2 Using two TITRONIC® 300 dispensers

Although the CMC measurements can be done by using one dispenser it is much more convenient to have two. When using two dispensers, one is to add water in the beaker and the other is to suck the solution out of the beaker. There are three advantages: First, you do not have to worry that the beaker is filled up since the volume in the beaker stays constant. Second, the contamination of bottles and tubings is not as big an issue since the filling Titronic is only using water and the removing one is removing waste. If the CMC measurements are done with different surfactant solutions, you do not have to clean the Titronic (which is quite laborious), instead you can just change the needles touching the solutions. And third, the amount of surfactant solution needed is typically less than when using only one Titronic, since the surfactant solution is only in the beaker.

1. Turn on the CMC measurement by clicking the icon. You need to select whether you want to measure with the ring or the plate. Either one can be used.

2. Put water into a bottle and connect it to the filling Titronic on the left **Note! Before you start the measurements, all the tubes of the Titronic have to be filled with water.**
    a. Fill the piston manually by pressing **fill** button on the dispenser. After the filling is done, Titronic will stop automatically.
    b. Let some surfactant solution out from the needle by pressing the **start/stop** button on the dispenser (put a cup under the needle). Dispense the surfactant solution as long as you can see air bubbles in the tubes. You can stop dispensing by pressing the **start/stop** on the dispenser again.
    c. Fill the piston one more time by pressing **fill** button on the dispenser.

3. Connect the removing Titronic on the right to a waste bottle. **Note! Before you start the measurements, all the tubes of the Titronic have to be filled with liquid.**
    a. Put some water into a beaker. Put the needle in water and press **fill** button on the dispenser**.** Titronic will now suck the water from the beaker and fill the needle.
    b. After filling press **start/stop** button on the dispenser. The water will now go to a waste bottle. Dispense water as long as you can see air bubbles in the tubes. You can stop dispensing by pressing **start/stop** button on the dispenser again. You may need to fill and dispense several times before all the air bubbles are gone.
    c. Fill the piston one more time by pressing **fill** button on the dispenser before starting the experiments.

4. Put a known volume and concentration of surfactant solution in the beaker. It is recommended to use at least 30 ml of solution.
   To calculate how much surfactant is needed for certain concentration, the equation

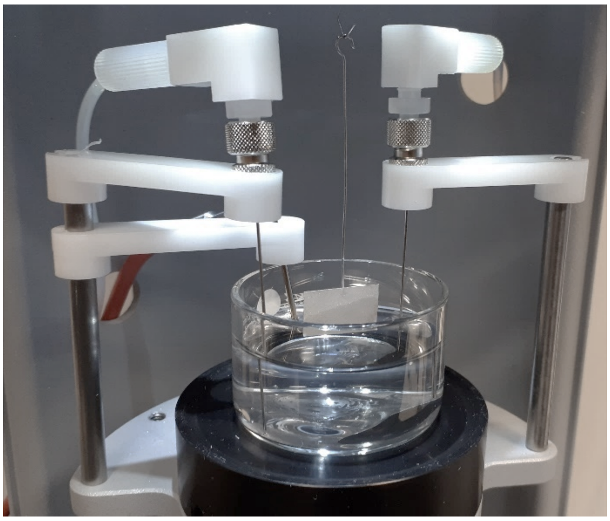
   $$m = M * V * c$$

   can be used, where m is the mass of the surfactant, M is the molar mass of the surfactant, V is the total volume and c is the concentration. Notice that the concentration has to be well above the CMC concentration of the surfactant.

5. Fill in the recipe
    a. Experiment name
    b. Check that the dimensions of the probe are correct
    c. Select the suitable vessel (in case of two titronics, this is not mandatory)
    d. Select the suitable light phase (in case of CMC air). Heavy phase is usually water (you can change the density of the solution if needed).
    e. Insert the volume of the heavy phase (= the volume of surfactant solution in the beaker). At least 30 ml should be used.
    f. Fill in the additional fields; concentration is the concentration of surfactant solution in the large bottle and is zero since only water is added. Initial concentration is the surfactant concentration in the beaker. Select the unit (depends on what unit you have used as concentration of surfactant solution).
    g. Select "Use two dispensers"

   h. You may want to change the stir after adding and wait after stirring times to be longer (e.g. 60 s) to ensure even distribution of surfactant molecules and a stable surface.

6. Attach the ring/plate to the hook. Put the beaker in its place and magnetic rod in the beaker (if stirrer is used). Put the needles in the beaker as well as temperature probe (if used). Bring the ring/plate close to the surface. Check that the ring/plate has enough space to lower into the solution, if not, adjust the needles.

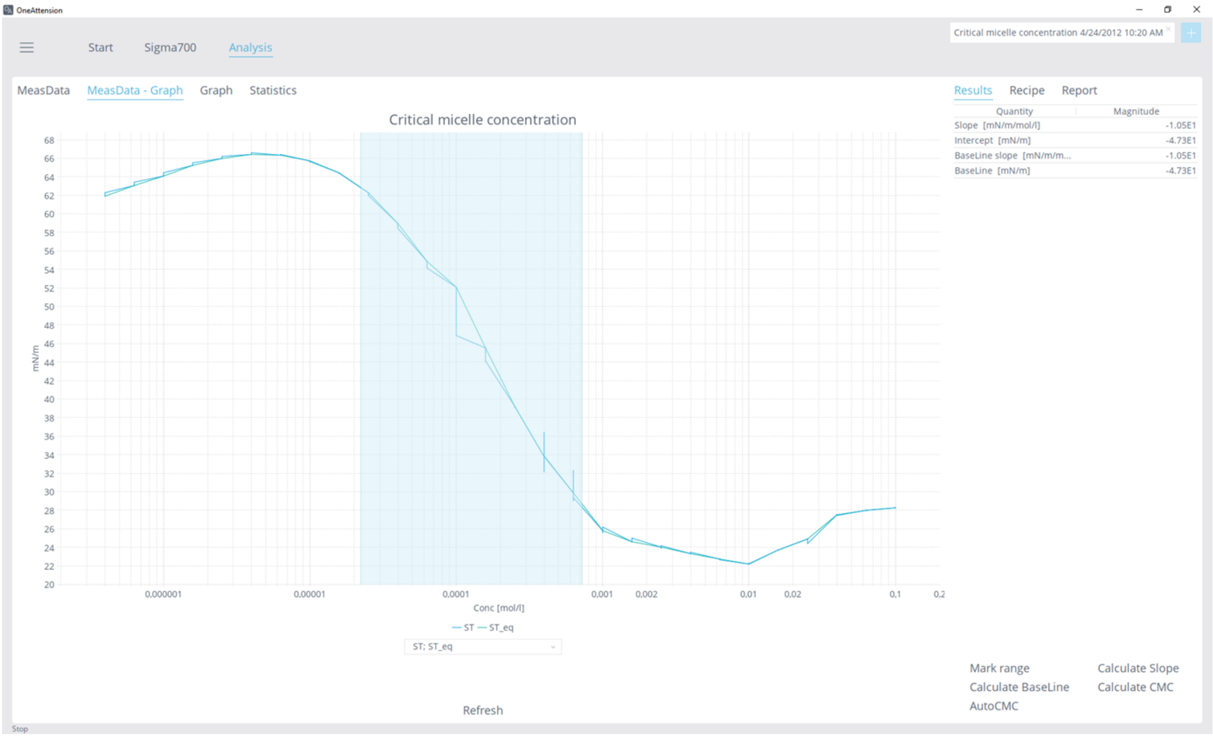


7. Press start.
8. The software will now tell you that you can change the start concentration and the end concentration. The start concentration is the initial concentration in the beaker and the end concentration the concentration when the measurement will be finished. These are calculated automatically by the software but can be changed if needed. If not press start again.

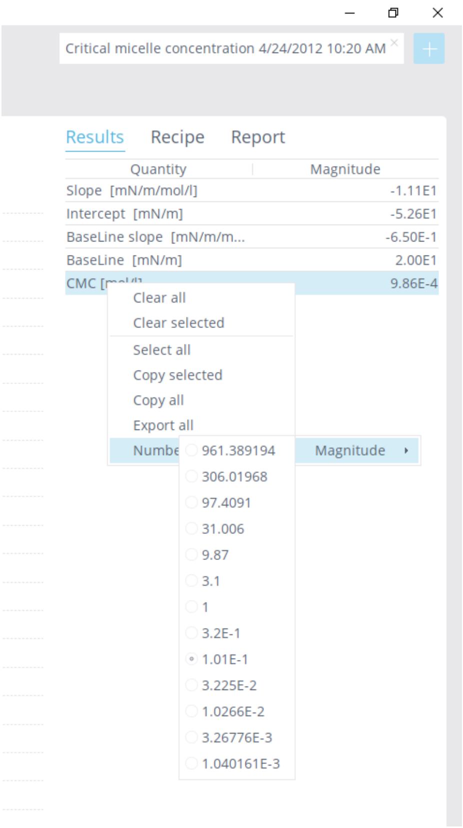
7.3 Analysis of the CMC data

The analysis of the CMC measurement is made the same way regardless of whether one or two dispensers were used. The CMC is automatically analyzed by the software but it can be also manually determined from the measurement data. The software determines the CMC by fitting two lines to the obtained CMC curve. Baseline is fitted to the plateau phase of the graph where surface tension has its minimum value as the surface is saturated by the surfactant molecules. Slope is fitted to the part where surface tension value changes linearly due to the changing amount of surfactant molecules at the surface. The CMC value is then obtained from the intercept of these two lines. To see the automatically calculated results, select the measurement you want to analyze and double click to open it. The calculated results table contains the analyzed slope, baseline, baseline slope, intercept and the CMC value. Slope and baseline lines are visible in the graph that shows surface tension as a function of concentration. For both automatic and manual analysis, you can set whether you allow tilt in the baseline analysis in the recipe.

To manually determine the CMC, open the graph that shows surface tension as a function of concentration. Press mark range. Mark the area by clicking the positions on the curve where the baseline should be drawn. This is the straight part of the curve when the surface tension is at its minimum value. Press Calculate BaseLine. Press Mark range again. Select the area of the curve where surface tension is decreasing linearly. Press Calculate Slope. Press Calculate CMC. The results are shown on the results tab. You can also go back to automatically analyzed results by clicking AutoCMC calculation button. Note that if the CMC is really small it might be that it is displayed as zero. If that happens, you should change the number formatting by highlighting the parameter you want to change. Click the right button and press number formatting → magnitude and select the appropriate way to present the results.



Quantity	Magnitude
Slope [mN/m/mol/l]	-1.05E1
Intercept [mN/m]	-4.73E1
BaseLine slope [mN/m/m...	-1.05E1
BaseLine [mN/m]	-4.73E1



Quantity	Magnitude
Slope [mN/m/mol/l]	-1.11E1
Intercept [mN/m]	-5.26E1
BaseLine slope [mN/m/m...	-6.50E-1
BaseLine [mN/m]	2.00E1
CMC [mol/l]	9.86E-4

8 Powder wettability measurement

Determination of contact angles for powders or porous solids requires at least two steps. First the material constant, C, must be assayed using a completely wetting liquid. Then the contact angles for other liquids can be measured using this C value. It is important that the solid samples be as identical as possible for each step. For porous solids you should attempt to use identical size samples. For powders you should use the same container and packing technique for each sample. To measure powder or porous solid contact angles you must also know the surface tension, density and viscosity of the liquid you are using for the measurement. More information can be found from the Theory section of this manual.

Many users may choose not to determine the material constant, C. Especially in cases where the main solid is the same, but it has been treated or coated differently. In such cases it might be sufficient to test the sample against the same one liquid and just compare the adsorption curves in order to see the effect of different coating procedures.

The first step in the measurement is to prepare the sample by packing the powder in a sample holder vessel or cut the porous solid to proper dimensions. Attension produces powder vessels ideally suited for this operation. The samples could also be fiber bundles or textiles.

To precede with the preparations of the measurement hang the vessel holding the powder or the porous test solid on the balance hook. At this point, it is advisable to drive the stage meant for holding the liquid vessel to its lowest position by using the Manual Membrane Keyboard. Make sure your measuring vessel holding the liquid is thoroughly cleaned. Then place the vessel containing the liquid on the stage. Next choose the Powder Wettability icon from the **Start tab**.

Your Wettability Measurement screen should appear as follows:

Powder default

Generic	
Basic Setup	
Probe	Powder probe, metal; WL = 50.8938 mm; ...
Vessel	Standard vessel
Materials	
Sample	
Material constant C [mm⁵]	0.000000
Light phase	Air
Heavy phase	Water 20 C
Control Parameters	
Probe Speed [mm/min]	20.00
Immersion Depth [mm]	0.50
Measurement Time [min]	5.00
Sample Interval [sec]	1.00
Detect Range [mN/m]	2.00
Return Position [mm]	5.00
Reset Speed [mm/min]	50.00
Wait after Target [sec]	0.00
Zero Balance at Target	☑
Stirrer Controls	
Stirrer Speed [%]	100
Start Stirrer on Start	☐
Stop Stirrer at Target	☐

Time	Mass² [g²]	Mass [g]

The powder wettability measurement contains the following parameter (in addition to generic parameters):

Basic setup

Probe: Here the details of the selected probe are listed. The probe can be selected from the database or the dimensions can be given manually. WL stands for "wetted length" and CF for "correction file"

Name: Name of the probe e.g. powder probe.

Type: Type of the probe can be selected from the list, for powder wettability "Round rod" is selected.

R (or plate width) [mm]: The radius of the powder container.

r (or plate thickness) [mm]: Not used in powder wettability measurements.

Correction file: Not used in powder wettability measurements.

Vessel: Details of the used vessel are listed here (not mandatory information for powder wettability measurement). Vessel can be chosen from the database or given manually.

Name: Name of the vessel, e.g. Standard vessel.

Diameter [mm]: The diameter of the vessel.

Volume [ml]: The volume of the vessel.

Materials

Sample: Here the information about the powder sample can be filled.

Name: Name of the sample

γ^{tot}: Total surface free energy.

γ^{d}: Dispersive component of the surface free energy.

γ^{+}: Base component of the surface free energy.

γ^{-}: Acid component of the surface free energy.

ρ: Density

Material constant C [mm^5]: Material constant is a parameter for the powder packing. It can be defined by measuring the powder wettability against some low surface tension liquid, which can assume to have zero contact angle against the powder.

Light Phase: The information about the light phase is listed here in details. The light phase can be chosen from the list or the information can be written. In case of powder wettability measurements, the light phase is air, this information is not however mandatory for the measurements.

Name: Name of the light phase, e.g. air.

γ^{tot}: Total surface tension.

γ^{d}: Dispersive component of the surface tension.

γ^{+}: Base component of the surface tension.

γ^{-}: Acid component of the surface tension

ρ: Density

η: Viscosity

Temperature [°C]: Temperature at which the parameters are defined.

Molecular weight [g/mol]: Molecular weight

Heavy Phase: The information about the heavy phase is listed here in details. In case the material constant or the contact angles are defined, density, surface tension and viscosity are mandatory information for the calculations.

Control Parameters

Probe speed [mm/min]: Speed at which the probe is moving

Immersion depth [mm]: The depth below the surface where the probe is immersed.

Meas time [min]: The measurement time. This can be changed also during the measurement.

Sample interval [sec]: How often the measurement data points are collected. Zero means as fast as possible (limited by the speed of the balance).

Detect range: Amount of change in force, which will register as contact with interface. If the liquid interface is detected before the actual contact of the probe has taken place, this value is set too low. If the surface is not detected, this value is set too high.

Return position: The position where the probe is returned to after the experiment.

Reset speed: The speed of the probe when not doing an experiment but controlling the probe manually.

Wait after Target [sec]: The waiting time before starting to collect data after the target depth has been reached.

Zero Balance at Target: If selected the balance is zeroed at the target depth.

Stirrer Controls

Stirrer speed [%]: The stirrer speed can be control here as a percentage from the maximum

Start stirrer on start: When selected, the stirrer will start when the start button is pressed.

Stop stirrer at target: When selected the stirrer is stopped when the target depth is reached.

8.1 Step by step instructions for a powder wettability measurement

1. The powder has to be packed to a special container. 1-2 g of powder is typically enough for the measurement. The packing should be done the same way every time, e.g. by tapping the container against a table three times. This is the key to achieving repeatable results.
2. Fill in the fields in the recipe or load a previously saved recipe:
   - Experiment name
   - Check that the selected probe is correct
   - Check that the light phase is correct (usually air)
   - Select the correct heavy phase (for the determination of material constant this has to be a liquid that completely wets the powder e.g. hexane) and check that surface tension, density and viscosity information is given.
3. Fill in the beaker with the heavy phase (e.g. hexane)
4. Bring the probe close to surface to save some measurement time, and press start.
5. After the measurement is completed, the software is able to calculate the material constant (see how the calculation is done from the analysis of the results section).
6. Remove the powder from the container, clean the container and put the new powder in.
7. Fill the beaker with the liquid of interest. **Note that this is a new heavy phase and should be filled in the recipe!**
8. Bring the probe close to surface to save some measurement time, and press start.
9. The device will stop automatically when the measurement time is past or the stop button is pressed.

When several powders are measured and compared to each other, material constant doesn't have to be measured. The measurements are done as indicated in the steps 7-9.

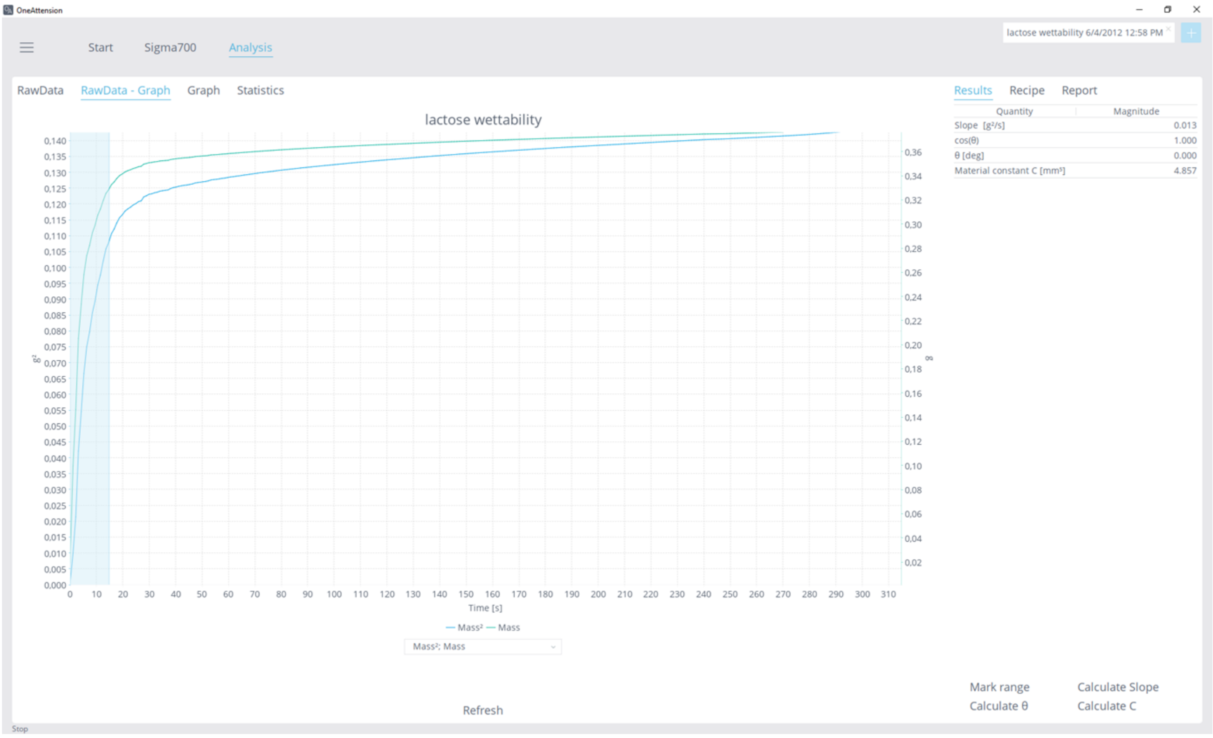
During the experiment, The Wettability Measurement window shows the measured Mass and Mass^2 of liquid adsorbed into the powder or porous solid sample vs. time graph, which will be updated and scaled as experiment progresses.

8.2 Analysis of the powder wettability data

To define the material constant, open the measurement that was done with hexane (or some other completely wetting liquid such as heptane).

Open the graph, press mark range. Press the start and end points for the range by clicking the curve. The range should be selected so that it is in the linear part of the curve. Press calculate slope followed by calculate C. The material constant is now calculated.

Open the measurement made with the same powder but some other liquid (e.g. water). Write the material constant in the recipe. Open the graph and mark the range same way as explained above. Press calculate slope followed by calculate θ. Contact angle is now calculated. Note that if the material constant is really small it might be that it is displayed as zero. If that happens, you should change the number formatting by highlighting the parameter you want to change. Click the right button and press number formatting → magnitude and select the appropriate way to present the results.



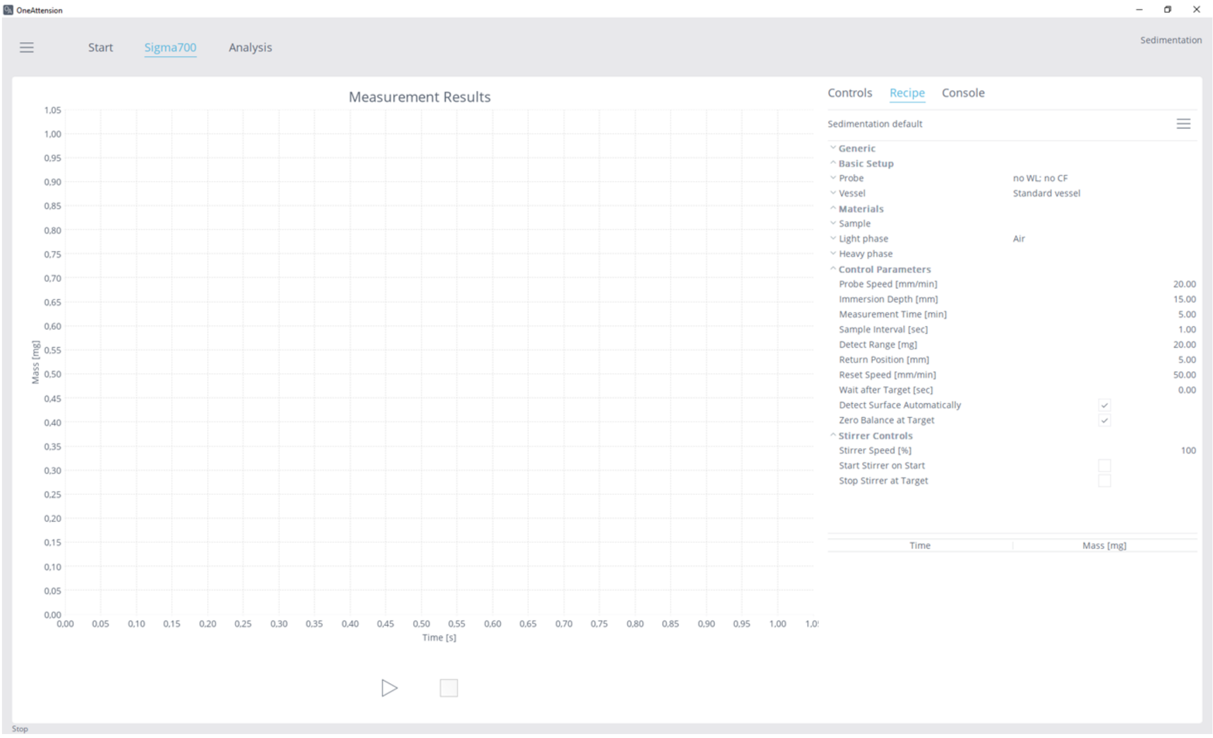
Quantity	Magnitude
Slope [g²/s]	0.013
cos(θ)	1.000
θ [deg]	0.000
Material constant C [mm⁵]	4.857

The contact angle calculation is not always needed but instead curves for different powder samples can be compared. Go to the table that shows all the data points. Press the right mouse button and select graph. Select time in the x-axis and mass in the y-axis. Press graph. Go to another measurement and do the same except this time select add to graph. The curve is added to the same graph as the previous one. Curve comparison shows both rate of the absorption (slope) and quantifies absorbed liquid.

9 Sedimentation measurement

Determination of sedimentation kinetics of solids in liquid is a rather straightforward measurement. The sedimentation probe i.e. round disk is immersed to a certain depth into the liquid containing the solid material while simultaneously mixing the liquid with a magnetic stirrer. After the magnetic stirrer is stopped the software records the amount of solid particles that sediments onto the disk in the liquid and records the Mass increase as a function of time.

To proceed with the preparations of the measurement hang the Sedimentation probe on the balance hook. At this point, it is advisable to drive the stage meant for holding the liquid vessel to its lowest position by using the Manual Membrane Keyboard. Prepare the sample liquid containing the solid material of interest and place it on the stage. Next click on the Sedimentation Measurement icon on the **Start tab**. Your Sedimentation Measurement screen should appear as follows:



Sedimentation default

Generic

Basic Setup

Probe	no WL; no CF
Vessel	Standard vessel

Materials

Sample	
Light phase	Air
Heavy phase	

Control Parameters

Probe Speed [mm/min]	20.00
Immersion Depth [mm]	15.00
Measurement Time [min]	5.00
Sample Interval [sec]	1.00
Detect Range [mg]	20.00
Return Position [mm]	5.00
Reset Speed [mm/min]	50.00
Wait after Target [sec]	0.00
Detect Surface Automatically	☑
Zero Balance at Target	☑

Stirrer Controls

Stirrer Speed [%]	100
Start Stirrer on Start	☐
Stop Stirrer at Target	☐

The sedimentation measurement contains the following parameters (in addition to generic field):

Basic setup

Probe: Here the details of the selected probe are listed. The probe can be selected from the database or the dimensions can be given manually. WL stands for "wetted length" and CF for "correction file". For sedimentation measurement, the selection of the probe is not needed.

Name: Name of the probe

Type: Type of the probe can be selected from the list

R (or plate width) [mm]: Not needed

r (or plate thickness) [mm]: Not needed

Correction file: Not needed.

Vessel: Details of the used vessel are listed here (not mandatory information for sedimentation measurement). Vessel can be chosen from the database or given manually.

Name: Name of the vessel, e.g. Standard vessel.

Diameter [mm]: The diameter of the vessel.

Volume [ml]: The volume of the vessel.

Materials

Sample: Here the information about the sedimentation sample can be filled.

Name: Name of the sample

γ^{tot}: Total surface free energy.

γ^{d}: Dispersive component of the surface free energy.

γ^{+}: Base component of the surface free energy.

γ^{-}: Acid component of the surface free energy.

ρ: Density

Light Phase: The information about the light phase is listed here in details. The light phase can be chosen from the list or the information can be written.

Name: Name of the light phase, e.g. air.

γ^{tot}: Total surface tension.

γ^{d}: Dispersive component of the surface tension.

γ^{+}: Base component of the surface tension.

γ^{-}: Acid component of the surface tension

ρ: Density

η: Viscosity

Temperature [°C]: Temperature at which the parameters are defined.

Molecular weight [g/mol]: Molecular weight

Heavy Phase: The information about the heavy phase is listed here in details. The parameters are as listed above for the light phase.

Control Parameters

Probe speed [mm/min]: Speed at which the probe is moving

Immersion depth [mm]: The depth below the surface where the probe is immersed.

Meas time [min]: The measurement time. This can be changed also during the measurement.

Sample interval [sec]: How often the measurement data points are collected. Zero means as fast as possible (limited by the speed of the balance).

Detect range: Amount of change in force, which will register as contact with interface. If the liquid interface is detected before the actual contact of the probe has taken place, this value is set too low. If the surface is not detected, this value is set too high.

Return position: The position where the probe is returned to after the experiment.

Reset speed: The speed of the probe when not doing an experiment but controlling the probe manually.

Wait after Target [sec]: The waiting time before starting to collect data after the target depth has been reached.

Detect surface automatically: When selected the balance is automatically zeroed when starting the measurement and the position is zeroed at the surface.

Zero Balance at Target: If selected the balance is zeroed at the target depth.

Stirrer Controls

Stirrer speed [%]: The stirrer speed can be control here as a percentage from the maximum

Start stirrer on start: When selected, the stirrer will start when the start button is pressed.

Stop stirrer at target: When selected the stirrer is stopped when the target depth is reached.

9.1 Step by step instructions for a sedimentation measurement

1. Put liquid in the beaker together with the material you want to investigate.
2. Fill in the fields in the recipe:
    - Experiment name
    - Define the wait time at target (this is the time that the device will stir your solution)
    - Mark "start stirrer at start" and "stop stirrer at target"
3. Put the sedimentation probe on the hook. Because the sedimentation probe is relatively wide, it has to be wetted before the measurement is started for it to be able to immerse below the surface of the liquid.
4. Press **start**. The magnetic stirrer goes on. The sedimentation probe will lower below the surface at the target depth indicated in the recipe. The stirring continues until the wait time is over. When stirrer stops, the balance will be zeroed automatically and the measurement will start. After the measurement time is finished, the recording of the mass will stop and the probe is lifted above the surface.

During the measurement, the Sedimentation Measurement window will show the measured Mass liquid adsorbed into the powder or porous solid sample vs. time graph, which will be updated and scaled as experiment progresses.

NOTE! It is possible that a mistake will be made while 'noticing' or detecting the interface. If the software reacts before actual contact of your probe with the interface has taken place the Detect Range in the Recipe is set too low. If the software does not react as the probe contacts the interface the Detect Range is set too high. It is advisable to monitor the start of the experiment to insure that the actual contact is detected.

9.2 Analysis of the sedimentation data

The sedimentation data is analyzed simply by looking at the mass vs. time graph and determining the rate of sedimentation.

10 Density measurement

Both liquid and solid density can be measured by using Sigma 700/701. The liquid density measurement will be performed in two stages: The volume of the density probe is determined against a liquid with known density (calibration step), hereafter the density of unknown liquids can be determined. The calibrated volume of the density probe is only temporarily recorded as long as the Density Measurement mode is active but can also be stored by saving the recipe. The measured density value is stored as a measurement and can be reviewed from the analysis part of the software. The solid density can be measured following the procedures: 1. Measure the weight of the solid in air, 2. Measure the weight in a known liquid, 3. The density of the solid can be calculated based on basic buoyancy calculations.

Density measurement contains the following parameters (in addition to generic fields):

Materials

Light Phase: The information about the light phase is listed here in details. The light phase can be chosen from the list or the information can be written.

Name: Name of the light phase, e.g. air.

γtot: Total surface tension.

γd: Dispersive component of the surface tension.

γ+: Base component of the surface tension.

γ-: Acid component of the surface tension

ρ: Density

η: Viscosity

Temperature [°C]: Temperature at which the parameters are defined.

Molecular weight [g/mol]: Molecular weight

Heavy Phase: The information about the heavy phase is listed here in details. The parameters are as listed above for the light phase.

Calibration liquid: a known liquid with which the density probe will be calibrated.

Control parameters

Probe Vol [cm3]: Volume of the density probe (is filled out automatically by the program after calibration of the density probe)

Probe Speed [mm/min]: Speed at which probe is lowered into the liquid

Immersion Depth [mm]: Depth to which the probe is lowered

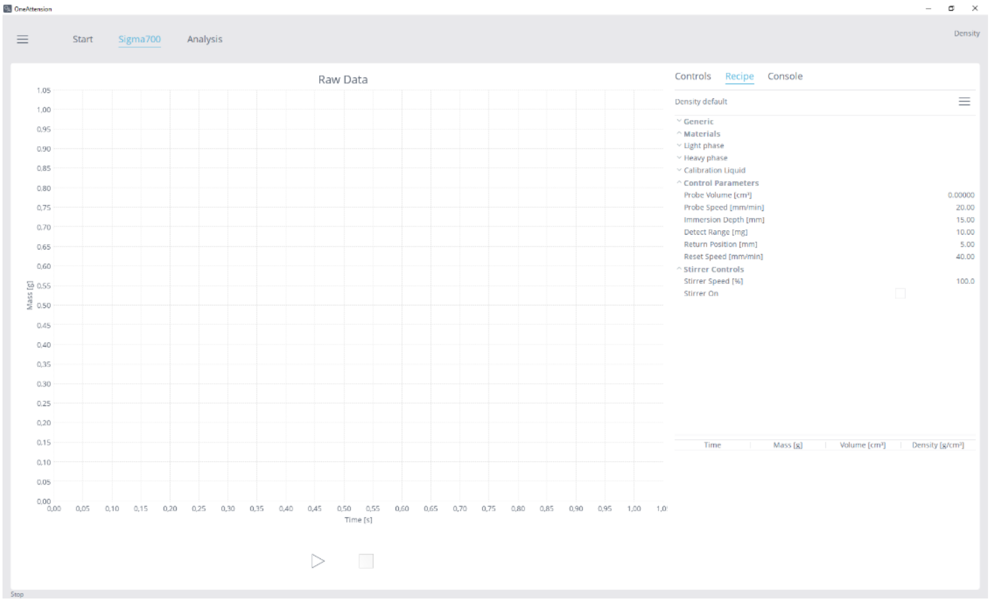
Detect range: Amount of mass change to indicate contact of the probe with the liquid interface

Return position: The position where the probe is returned to after the experiment.

Reset speed: The speed of the probe when not doing an experiment but controlling the probe manually.

10.1 Step by step instructions for liquid density measurement

1. To measure liquid density, select liquid density measurement from the start menu, and the following density measurement screen should appear:



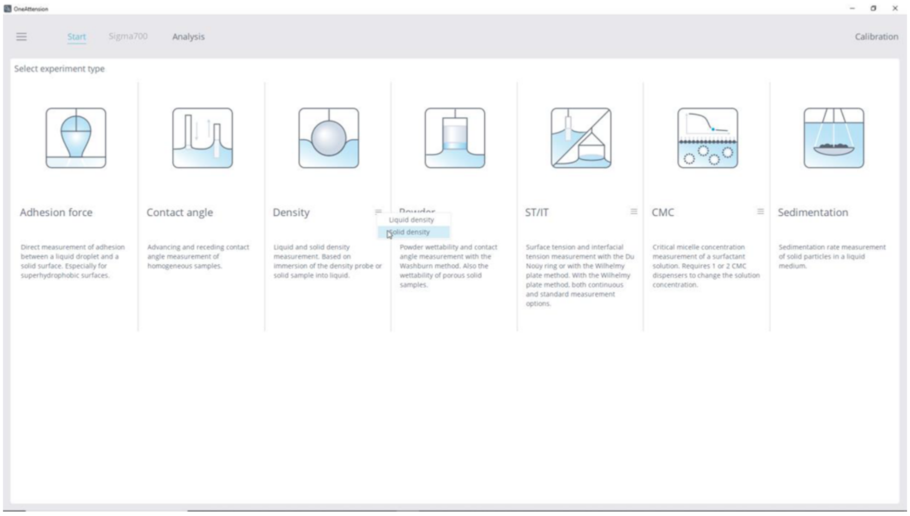
Density default

- Generic
- Materials
  - Light phase
  - Heavy phase
  - Calibration Liquid
- Control Parameters
  - Probe Volume [cm³] 0.00000
  - Probe Speed [mm/min] 20.00
  - Immersion Depth [mm] 15.00
  - Detect Range [mg] 10.00
  - Return Position [mm] 5.00
  - Reset Speed [mm/min] 40.00
- Stirrer Controls
  - Stirrer Speed [%] 100.0
  - Stirrer On ☐

2. Then you have to fill the empty fields in the default recipe; experiment name and the calibration liquid. The calibration liquid is most commonly water, but some other liquid can also be used. The calibration liquid can be selected from the software database.
3. Put the calibration liquid into the beaker (usually water). Note that there should be enough water that the density probe will be completely covered without touching the bottom of the beaker. Hang the cleaned calibration probe (Note! Do not burn it with Bunsen burner, use e.g. ethanol instead). Bring the calibration probe close to surface, to save time. Press calibrate.
4. After the calibration is completed, change the liquid in the beaker to one you want to measure. Again there should be enough liquid for probe to be immersed completely. Clean the probe again, hang it on the hook and bring close to surface. Press start.
5. You can measure the density of another liquid without making the calibration, as long as you do not turn off the density measurement in between. It is possible to save the calibration factor by saving the recipe.

10.2 Step by step instructions for solid density measurement

1. To measure solid density, select solid density measurement from the start menu.



Adhesion force: Direct measurement of adhesion between a liquid droplet and a solid surface. Especially for superhydrophobic surfaces.

Contact angle: Advancing and receding contact angle measurement of homogeneous samples.

Density: Liquid and solid density measurement. Based on immersion of the density probe or solid sample into liquid.

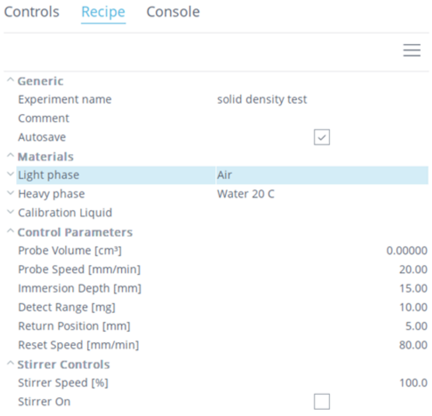
Powder: Powder wettability and contact angle measurement with the Washburn method. Also the wettability of porous solid samples.

ST/IT: Surface tension and interfacial tension measurement with the Du Noüy ring or with the Wilhelmy plate method. With the Wilhelmy plate method, both continuous and standard measurement options.

CMC: Critical micelle concentration measurement of a surfactant solution. Requires 1 or 2 CMC dispensers to change the solution concentration.

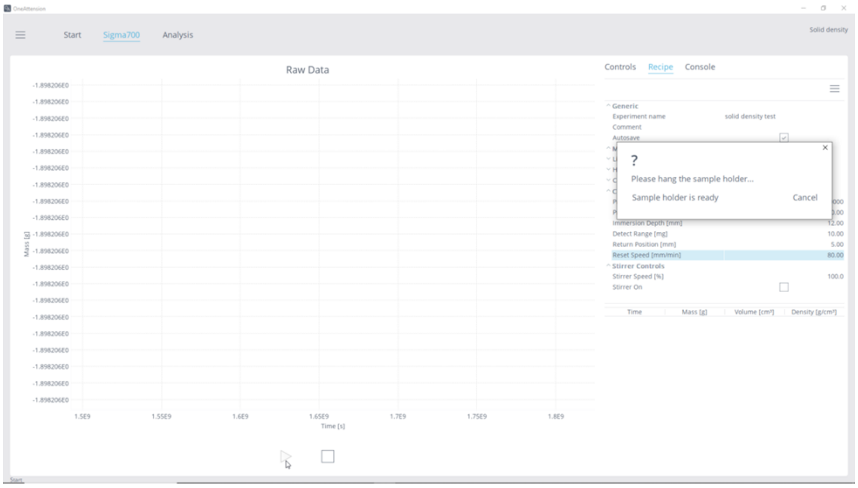
Sedimentation: Sedimentation rate measurement of solid particles in a liquid medium.

2. In the recipe, fill in the experiment name, the light and heavy phase information. The heavy phase is the liquid you are using in the measurements (typically water) and light phase is air. Set also the immersion depth which is the height of your sample. You might also need to adjust the detect range to be lower depending on your sample.



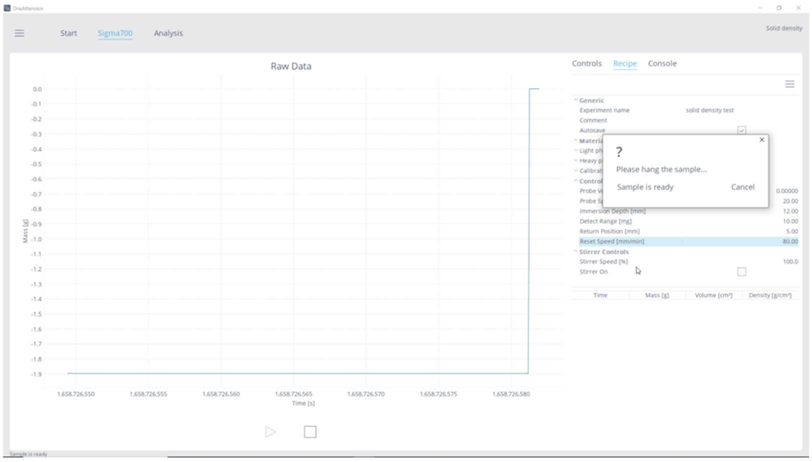
Generic
Experiment name solid density test
Comment
Autosave ☑
Materials
Light phase Air
Heavy phase Water 20 C
Calibration Liquid
Control Parameters
Probe Volume [cm³] 0.00000
Probe Speed [mm/min] 20.00
Immersion Depth [mm] 15.00
Detect Range [mg] 10.00
Return Position [mm] 5.00
Reset Speed [mm/min] 80.00
Stirrer Controls
Stirrer Speed [%] 100.0
Stirrer On ☐

3. Press start. The software will now ask you to place holder for the sample to the hook. If you place the sample directly to the hook, you can click sample holder ready when the hook is empty.



?
Please hang the sample holder...

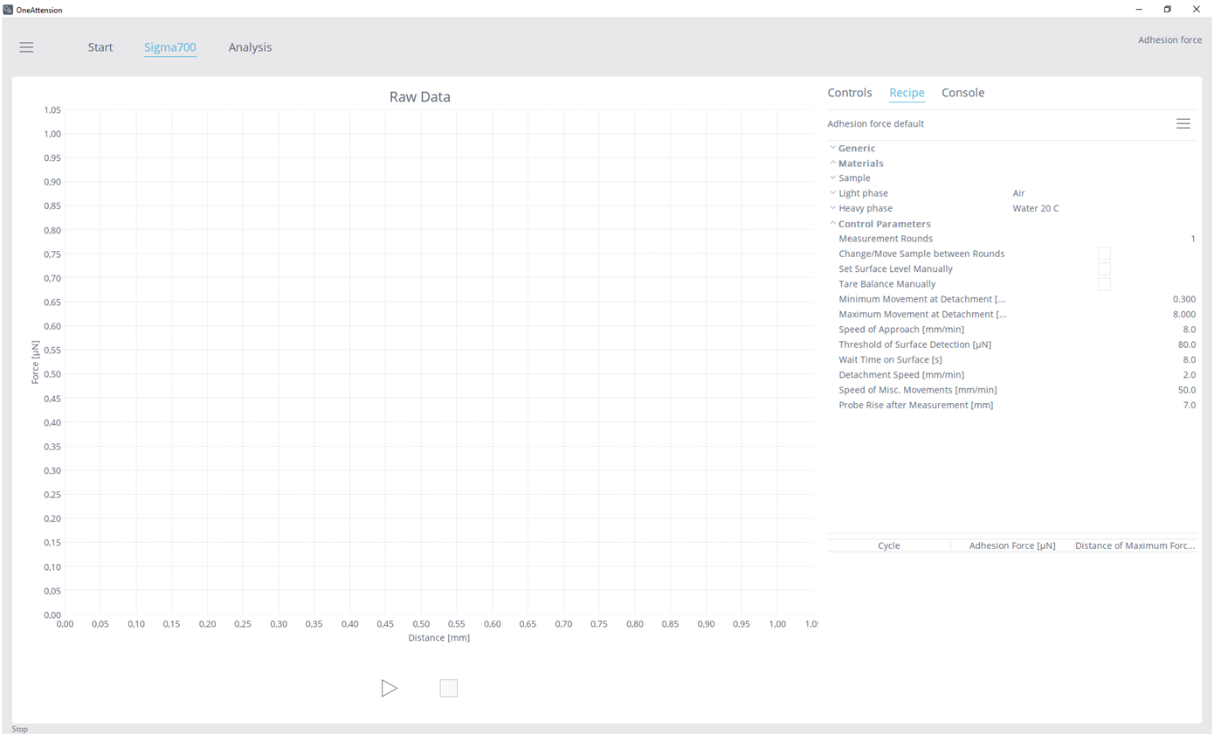
4. The software will then ask you to place the sample. You can remove the sample holder from the hook to place the sample if needed, or you can hang the sample directly to the holder or on the hook. After hanging the sample, bring the liquid level close to the sample to shorten the measurement time.
5. Press sample is ready when done. The measurement is now performed automatically.



?
Please hang the sample...

11 Adhesion force measurement

To start the measurement, choose Adhesion force icon on the **Start tab**. The following Adhesion Force screen should appear:



Adhesion force default

Generic

Materials

Sample

Light phase Air

Heavy phase Water 20 C

Control Parameters

Measurement Rounds	1
Change/Move Sample between Rounds	☐
Set Surface Level Manually	☐
Tare Balance Manually	☐
Minimum Movement at Detachment [...	0.300
Maximum Movement at Detachment [...	8.000
Speed of Approach [mm/min]	8.0
Threshold of Surface Detection [µN]	80.0
Wait Time on Surface [s]	8.0
Detachment Speed [mm/min]	2.0
Speed of Misc. Movements [mm/min]	50.0
Probe Rise after Measurement [mm]	7.0

Cycle	Adhesion Force [µN]	Distance of Maximum Forc...

Adhesion force measurement will show the adhesion force versus distance from surface curve. The method is mainly applicable for superhydrophobic surfaces as the drop needs to separate from the surface during measurement for best results.

Adhesion force measurement contains the following parameters (in addition to generic fields):

Materials

Light Phase: The information about the light phase is listed here in details. The light phase can be chosen from the list or the information can be written.

Name: Name of the light phase, e.g. air.

γ^{tot}: Total surface tension.

γ^{d}: Dispersive component of the surface tension.

γ^{+}: Base component of the surface tension.

γ^{-}: Acid component of the surface tension

ρ: Density

η: Viscosity

Temperature [°C]: Temperature at which the parameters are defined.

Molecular weight [g/mol]: Molecular weight

Heavy Phase: The information about the heavy phase is listed here in details. The parameters are as listed above for the light phase.

Control parameters

Measurement rounds: Number of consecutive measurements.

Change/Move sample between rounds: Choose if you wish to perform different measurement rounds on different samples.

Set surface level manually: Choose if you wish to manually show the software where the solid surface is (otherwise the level is found automatically).

Tare balance manually: Choose if you wish to manually tare the balance (otherwise the balance is tared automatically between rounds).

Minimum movement at detachment [mm]: The minimum moving distance before the measurement can end.

Maximum movement at detachment [mm]: The maximum moving distance before the measurement can end.

Speed of Approach [mm/min]: The speed of the probe when approaching the surface.

Threshold of Surface Detection [μN]: The amount of force change required for determining the surface level.

Wait time on surface [s]: Wait time on surface before detachment pull.

Detachment Speed [mm/min]: The speed of the probe when detaching from the surface.

Speed of Misc Movements [mm/min]: The speed of the probe in other motions except approach and detachment.

Probe rise after measurement [mm]: The height where the probe will be taken after the measurement is complete.

11.1 Step by step instructions for an adhesion force measurement

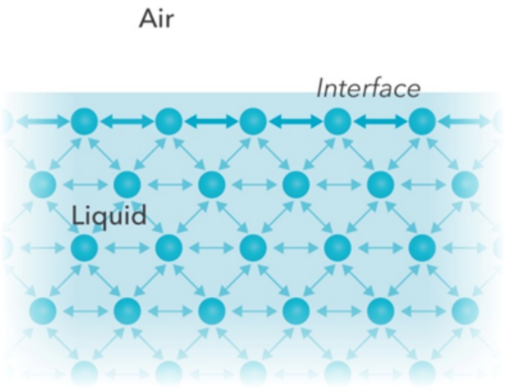
1. First you have to fill the empty fields in the default recipe like experiment name. Adjust control parameters as needed.
2. Hang the cleaned adhesion force probe on the hook. Soak the head of the probe in water to attach a droplet to it. Insert your solid sample onto the sample stage. Bring the adhesion force probe close to surface, to save time. Press Start.

12 Theory

This chapter contains information about the theory behind the measurements.

12.1 Surface and interfacial tension

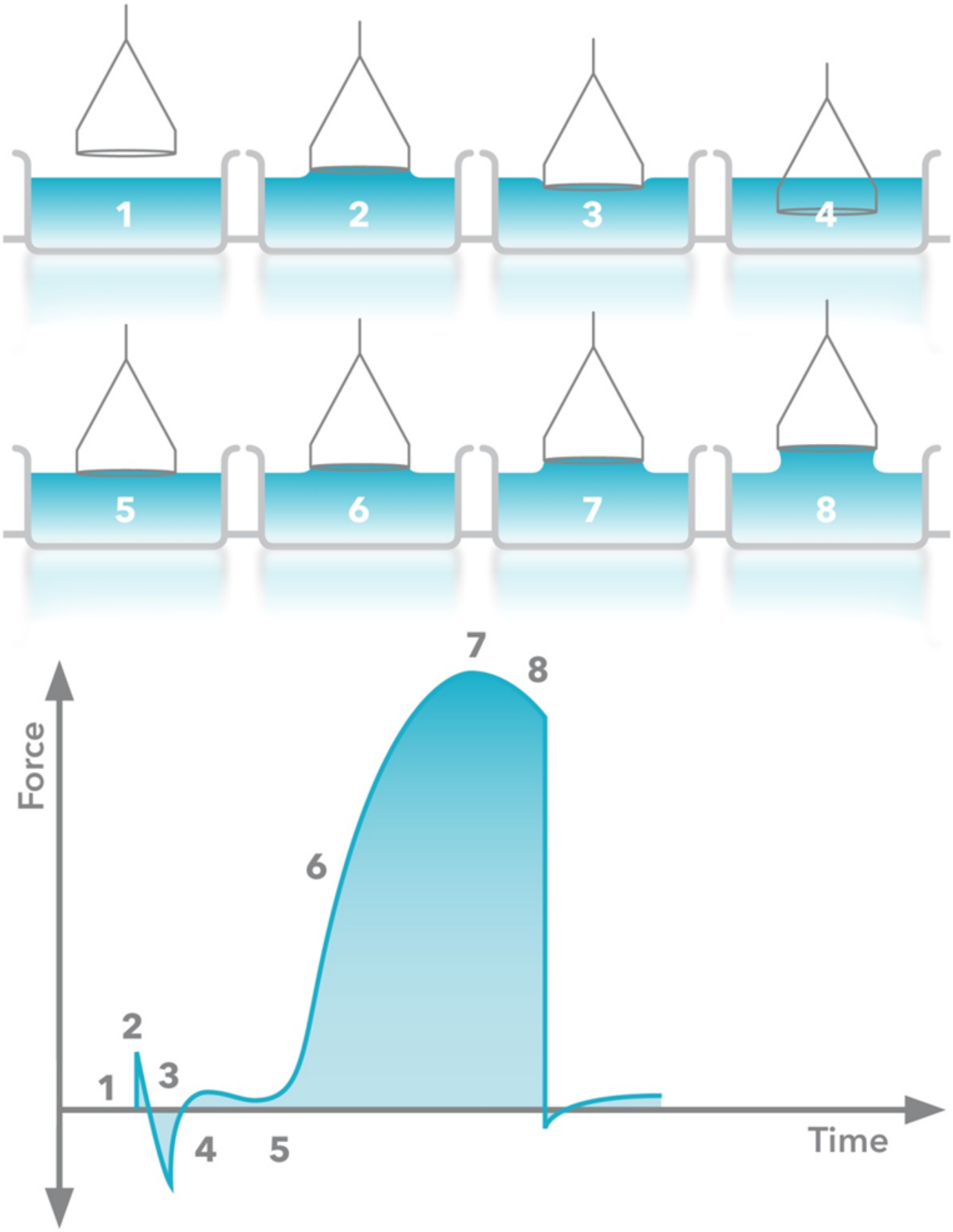
The cohesive forces between liquid molecules are responsible for the phenomenon known as surface tension (ST). The molecules at the surface do not have the similar neighboring atoms on all sides and thus they cohere more strongly to those directly associated with them on the surface. This forms a surface "film" which makes it more difficult to move an object through the surface than move it when it is completely immersed. The same situation applies also at the interface of the two liquids that do not mix together. In this case, the term interfacial tension (IFT) is used. There are several different units for surface and interfacial tension; typically mN/m (which is equivalent to dynes/cm) is used.



The measurement of the surface and interfacial tension can be done by using Sigma force tensiometer. It is based on the force measurements of the interaction of a probe with the surface or interface of two liquids. A probe is hang on the balance and brought into contact with the liquid interface tested. The forces experienced by the balance as the probe interacts with the surface of the liquid can be used to calculate the surface tension. The forces present in this situation depend on the following factors; size and shape of the probe, contact angle between the probe and the liquid and surface tension of the liquid. The size and the shape of the probe are easily controlled. The probe is made of platinum which ensures the zero contact angle between the probe and the liquid to be studied. Two types of probes are commonly used; the Du Noüy ring and the Wilhelmy plate. A metal rod can also be used when the sample volume is limited.

Du Noüy ring

This method utilizes the interaction of a platinum ring with the surface of the liquid. The ring is submerged below the interface by moving the stage where liquid container is placed. After immersion, the stage is gradually decreased and the ring pulls up the meniscus of the liquid. Eventually this meniscus tears from the ring. Prior to this event, the volume (and thus the force exerted) of the meniscus passes through the maximum value and begins to drop before the actual tearing event.



In the Figure above, different stages of the experiment can be identified.

1. The ring is above the surface and the force is zeroed.
2. The ring hits the surface and there a slight positive force due to the adhesive force between the ring and the surface.
3. The ring must be pushed through the surface (due to surface tension) which causes a small negative force.
4. The ring breaks the surface and a small positive force is measured due to the supporting wires of the ring.
5. When lifted through the surface the measured force starts to increase.
6. The force keeps increasing until
7. The maximum force is reached.
8. After the maximum there is a small decrease of the force until the lamella breaks (or the ring is pushed back below the surface).

The calculation of the surface or interfacial tension by this technique is based on the measurement of this maximum force. The depth of immersion of the ring and the level to which the ring is raised when it experiences the maximum pull are irrelevant to this technique. The original calculations are based on the ring with the infinite diameter (or wire) and do not consider the excess liquid that is pulled up due to the proximity of one side of the ring to the other. Nowadays correction factors are routinely used [Huh Maison]. For the utilization of the correction factor, the density of the liquid has to be known.

Wilhelmy plate

This method utilizes the interaction between the platinum plate (= the probe) and the surface of the liquid. The calculations of this technique are based on the geometry of the fully wetted plate in contact with the liquid. In this method the position of the probe relative to the surface is significant. As the surface is brought in contact with the probe, instrument will detect this by the change in force it experiences. It will register the height at which this occurs and set it to be “zero depth of immersion”. The plate is then wetted to a set depth. When the plate is later returned to the zero depth of immersion, the force is registered and used to calculate the surface tension according to equation.

$$Wetting\ force = \gamma_l P cos\theta$$

Remember that the term cosθ goes to 1 since the contact angle between the probe and the liquid is considered to be zero.

Platinum rod

Both of the above mentioned approaches require a relatively large amount of the liquid to be used to ensure complete wetting of the probe. It is possible to use a sample vessel with the smaller diameter to decrease the volume of the liquid. Limitation to this strategy occurs when the edges of the probe approach the edges of the measuring vessel. When the edges are too close to each other, the balance can be affected by the meniscus that forms between the liquid and the edge of the vessel.

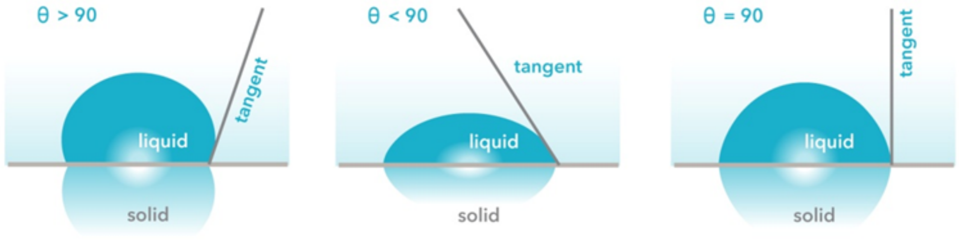
To avoid this problem, it is possible to use the platinum rod which allows you to use much smaller in diameter sample vessel and thus less volume of the sample. In any of these techniques the accuracy of the measurement is affected by the accuracy of the geometry of your probe. The geometry of the fine probe is likely to be less accurate than the geometry of the ring or the plate which will lead to bigger error percentage of the surface/interfacial tension results. Therefore this approach should only be used when the volume of the sample is limited. Calculations are based on the same principle as the Wilhelmy plate method.

12.2 (Dynamic) contact angle

Contact angle, θ, is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect. The well-known Young equation describes the balance at the three phase contact of solid-liquid and gas.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} cos\theta_Y$$

The interfacial tensions, γ_{sv}, γ_{sl} and γ_{lv}, form the equilibrium contact angle of wetting, many times referred as Young contact angle θ_Y.



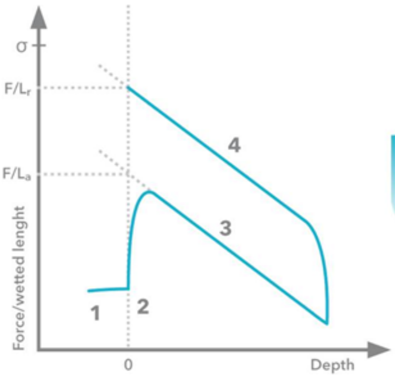
From figure above, it can be seen that the low contact angle values indicate that the liquid spreads on the surface while high contact angle values show poor spreading. If the contact angle is less than 90 ° it is said that the liquid wets the surface, zero contact angle representing complete wetting. If contact angle is greater than 90 °, the surface is said to be non-wetting with that liquid. Contact angles can be divided into static and dynamic angles. Static contact angles are measured when droplet is standing on the surface and the three phase boundary is not moving. Static contact angles are utilized in quality control and in research and product development. Contact angle measurements are used in fields ranging from printing to oil recovery and coatings to implants.

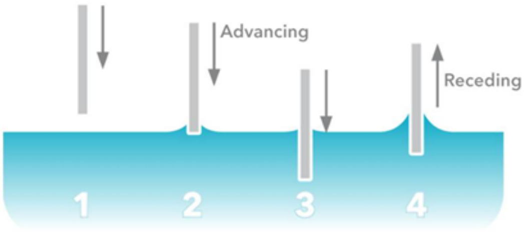
When the three phase boundary is moving dynamic contact angles can be measured, and are referred as advancing and receding angles. Contact angle hysteresis is the difference between the advancing and receding contact angles. Contact angle hysteresis arises from the chemical and topographical heterogeneity of the surface, solution impurities absorbing on the surface, or swelling, rearrangement or alteration of the surface by the solvent. Advancing and receding contact angles give the maximum and minimum values the static contact angle can have on the surface. Difference between advancing and receding angles can be as high as 50 °. Dynamic contact angles and contact angle hysteresis has become a popular topic because of the recent interest in superhydrophobic and self-cleaning surfaces [1,2]. Hysteresis is however also important in other situations such as intrusion of water into porous media, coating, and adsorption at liquid/solid interface.

Dynamic contact angles can be measured by using Sigma force tensiometer. Force tensiometer measures the mass affecting to the balance when a sample of solid is brought in contact with a test liquid. The contact angle can then be calculated by using the equation below when surface tension of the liquid (γ_l) and the perimeter of the sample (P) are known.

$$Wetting\ force = \gamma_l P cos\theta$$

In Figure below, a complete contact angle measurement cycle is presented. As can be seen, with force tensiometer the measured contact angle is always dynamic contact angle since the sample is moving against the liquid. When the sample is emerged on the liquid the advancing contact angle is recorded and when the sample is emerging the receding contact angle is measured.





12.3 Surface free energy

Precise characterization of solid material surfaces plays a vital role in research and product development in many industrial and academic areas. Wettability of the surface is important in processes like painting and printing, and has been utilized in the study of biomaterial –cell interactions to name a few. Wettability can be studied by measuring contact angle of the substrate with given liquid. The well-known Young equation describes the balance at the three phase contact of solid-liquid and gas.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} cos\theta_Y \qquad (1)$$

The interfacial tensions, γ_{sv}, γ_{sl} and $\gamma_{lv,}$ form the equilibrium contact angle of wetting, many times referred as Young contact angle θ_Y. The Young equation assumes that the surface is chemically homogenous and topographically smooth. One of the important applications of the contact angle measurement is the assessment of the surface free energy (SFE) of the solid. Surface free energy of the solid is equivalent to surface tension of the liquid and the unit is the same mN/m (= dynes/cm). Although contact angle itself also gives indications on the wetting properties of the surface, contact angle always depends also on the liquid used for the measurements.

In equation (1), the surface free energy of the solid is described by using the contact angle θ_Y, surface tension of the liquid γ_{lv} and interfacial tension between solid and liquid γ_{sl}. The first two are easily measured but the problem is the unknown γ_{sl} which cannot be measured directly. To be able to solve the equation, more assumptions of the relationship between γ_{sv}, γ_{sl} and γ_{lv} has to be made.

To be able to understand the different methods, term "work of adhesion" has to be explained. Thermodynamic adhesion is the work required to separate surfaces into two new surfaces (see Figure 1(a)). The equation for work of adhesion can be written as

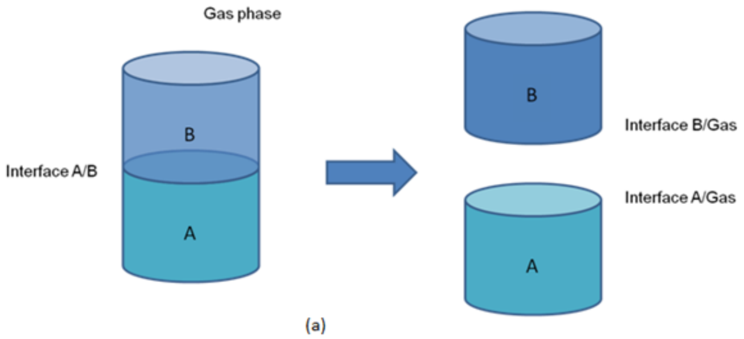
$$W_A = \gamma_A + \gamma_B - \gamma_{AB} \qquad (2)$$

where γ_{AB} is the interfacial tension between two phases, γ_A is the surface tension of phase A and γ_B is the surface tension of phase B. Now, if the other phase is solid and other liquid the equation can be written as

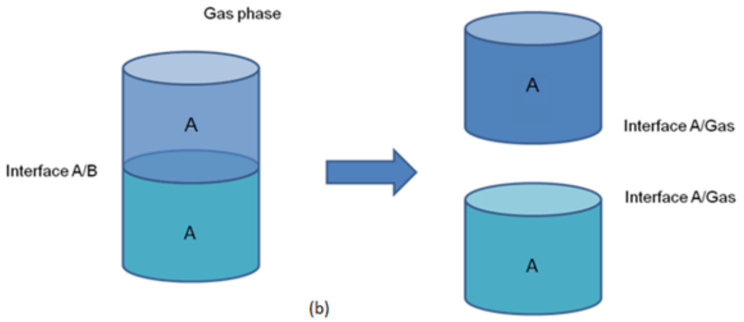
$$W_{sl} = \gamma_{lv} + \gamma_{sv} - \gamma_{sl} \qquad (3)$$

Equations (1) and (3) can be combined into Young-Dupré equation

$$W_{sl} = \gamma_{lv}(1 + cos\theta_Y) \qquad (4)$$



(a)



(b)

In a similar way the work of cohesion can be defined as shown in the Figure (b) above.

$$W_C = \gamma_A + \gamma_A - 0 = 2\gamma_A \qquad (5)$$

Berthelot initiated the direction to surface free energy calculations at the end of 19th century. He assumed that the work of adhesion (WA) between the solid and liquid is equal to the geometric mean of the cohesion work of a solid and the cohesion work of the measuring liquid.

$$W_{sl} = \sqrt{(W_{ss}W_{ll})} \qquad (6)$$

And then combining with the equations (4), (5) and (6)

$$W_{sl} = \sqrt{2\gamma_{lv}2\gamma_{sv}} = 2\sqrt{\gamma_{lv}\gamma_{sv}} = \gamma_{lv}(1 + cos\theta_Y) \qquad (7)$$

Equation (7) is the basis for the following SFE theories.

Equation of state

Although there are few different formulas based on Equation of state (EQS), the best known is one described by Neumann

$$cos\theta_Y = -1 + 2\sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}}e^{-\beta(\gamma_{lv}-\gamma_{sv})2} \qquad (8)$$

Here the coefficient $\beta = 0.0001247$ is determined experimentally. In principle the equation of state requires the measurement to be done only by using one liquid and regardless which liquid is chosen the surface free energy result should be the same. There is a lot of criticism against this theory. The controversy deals with the question whether the constant β is universal constant of the materials or just quantity obtained as a result if the iterative procedures applied. Equation of state theory also does not divide the surface tension into different components as the other theories.

OWRK/Fowkes

The idea of division of the SFE into individual components includes the assumption that γ_{sl} is determined by various interfacial interactions that depend on the properties of both the measured substrate and the measurement liquid. Fowkes assumed that surface free energy of a solid (and surface tension of a liquid) is a sum of independent components, associated with specific interactions:

$$\gamma_{sv} = \gamma_{sv}^{d} + \gamma_{sv}^{p} + \gamma_{sv}^{h} + \gamma_{sv}^{i} + \gamma_{sv}^{ab} + \gamma_{s}^{o} \qquad (9)$$

where γ_{sv}^{d}, γ_{sv}^{p}, γ_{sv}^{h}, γ_{sv}^{i} and γ_{sv}^{ab} are the dispersion, polar, hydrogen, induction and acid-base components, respectively. γ_{sv}^{o} refers to all remaining interactions. Fowkes investigated mainly systems containing substance (solid or liquid) in which only the dispersion interactions appear. According to Fowkes, dispersion interactions are connected with London interactions, arising from the electron dipole fluctuations. Owen and Wendt continued the Fowkes idea stating that all to components in the right side of equation (9), except γ_{sv}^{d} can be considered polar (γ_{sv}^{p}). Consequently, leading to equations (10).

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{\gamma_{sv}^{d}\gamma_{lv}^{d}} - 2\sqrt{\gamma_{sv}^{p}\gamma_{lv}^{p}} \qquad (10)$$

And if combined with Young equation (1), equation called OWRK can be written as

$$\sqrt{\gamma_{sv}^{d}\gamma_{lv}^{d}} + \sqrt{\gamma_{sv}^{p}\gamma_{lv}^{p}} = 0.5\,\gamma_{lv}(1 + cos\theta_{Y}) \qquad (11)$$

Because there are two unknowns, γ_{sv}^{d} and γ_{sv}^{p} , in equation (11), two liquids with the known dispersive and polar components are needed to solve it. The liquid with the dominant polar component should be chosen as one measuring liquid and dispersive liquid as other one. Water, glycerol and formamide can be used as polar liquids and diiodomethane and α-bromonaphtalene as dispersive. Water and diiodomethane are most often utilized. OWRK is one of the most common methods for SFE calculations.

Wu

Wu accepted to idea of Owen and Wendt to divide the SFE into polar and dispersive components. Instead of using the geometric mean as in equation (10), he used the harmonic one.

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 4\left[\frac{\gamma_{sv}^{d}\gamma_{lv}^{d}}{(\gamma_{sv}^{d} + \gamma_{lv}^{d})} + \frac{\gamma_{sv}^{p}\gamma_{lv}^{p}}{(\gamma_{sv}^{p} + \gamma_{lv}^{p})}\right] \qquad (12)$$

And if combined with Young equation (1), Wu equation can be written as

$$\left[\frac{\gamma_{sv}^{d}\gamma_{lv}^{d}}{(\gamma_{sv}^{d} + \gamma_{lv}^{d})} + \frac{\gamma_{sv}^{p}\gamma_{lv}^{p}}{(\gamma_{sv}^{p} + \gamma_{lv}^{p})}\right] = 0.25\gamma_{lv}(1 + cos\theta_{Y}) \qquad (13)$$

As in the OWRK method, Wu method requires the use of at least two liquids, one mainly polar and one dispersive. Water and diiodomethane are again often used. From a theoretical point of view, the geometric mean is more accurate than the harmonic one.

Acid-base

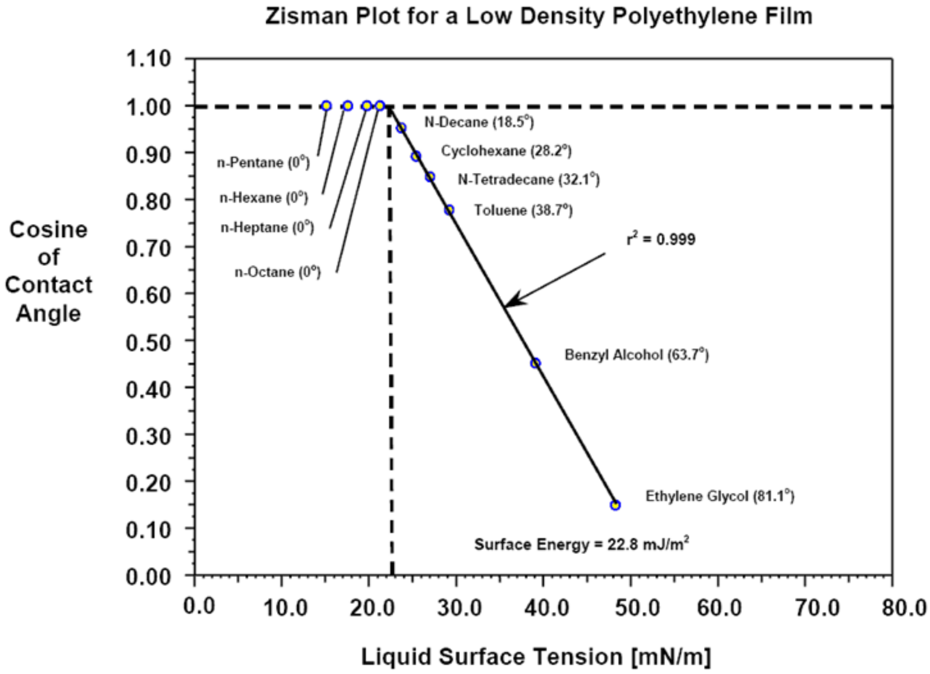
By using the acid-base approach, sometimes called Van Oss-Chaudhury-Good method, the polar component is further divided into acid and base components and the equation can be written as

$$\sqrt{\gamma_{sv}^{d}\gamma_{lv}^{d}} + \sqrt{\gamma_{sv}^{acid}\gamma_{lv}^{base}} + \sqrt{\gamma_{sv}^{base}\gamma_{lv}^{acid}} = 0.5\,\gamma_{lv}(1 + cos\theta_{Y}) \qquad (14)$$

Since there are three unknown, γ_{sv}^{d}, γ_{sv}^{acid} and γ_{sv}^{base}, at least three liquids with known properties are needed to solve the equation. One dispersive (e.g. diiodomethane) and two polar (e.g. water glycerol) should be used. Acid-base method is one of the most recent developments in the field of SFE calculations. It has a potential to give more in depth information about surface properties of the solid but has been criticized by its sensitivity to even small variations in the contact angle measurements or properties of liquids used.

Zisman plot

Zisman plot is used to define so-called critical surface tension which is the surface tension of the liquid needed to complete wet the solid (contact angle between the solid and liquid is zero). This critical surface tension value differs from the surface free energy of the solid, and is not divided into dispersive and polar components. In practice, critical surface tension is defined by measuring the contact angle between several different probe liquids and the studied surface. The results are then plot by having cosθ in y-axis and the surface tension of the liquid in x-axis. Straight line is then fitted to this measurement points and extrapolated to point cosθ=1 which will then give the critical surface tension value for the surface. In theory, only two measurement points would be needed but in practice using just few different liquids will lead to incorrect results, even negative values are often seen. At present, this method is not commonly used due to insufficient theoretical justification and laborious investigation procedure.



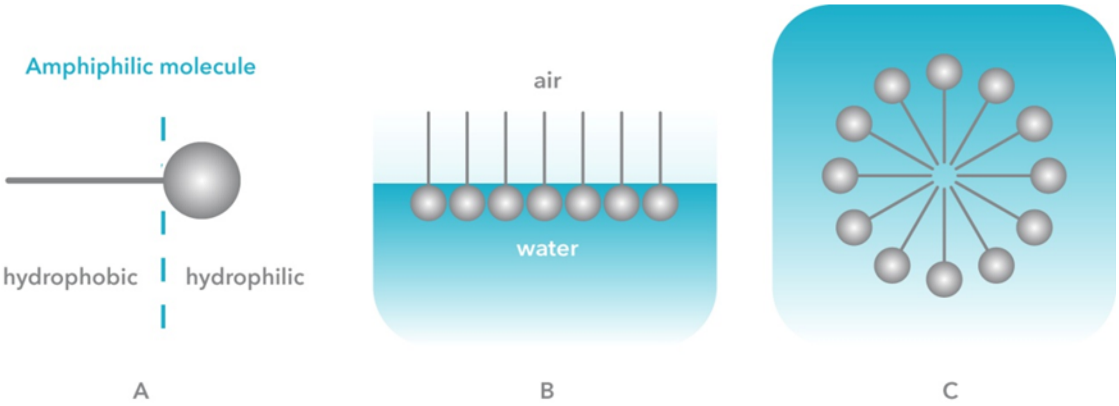
References:

[1] L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang and D. Zhu, "Superhydrophobic surfaces: From natural to artificial" , Advanced materials 14 (2002) 1857.

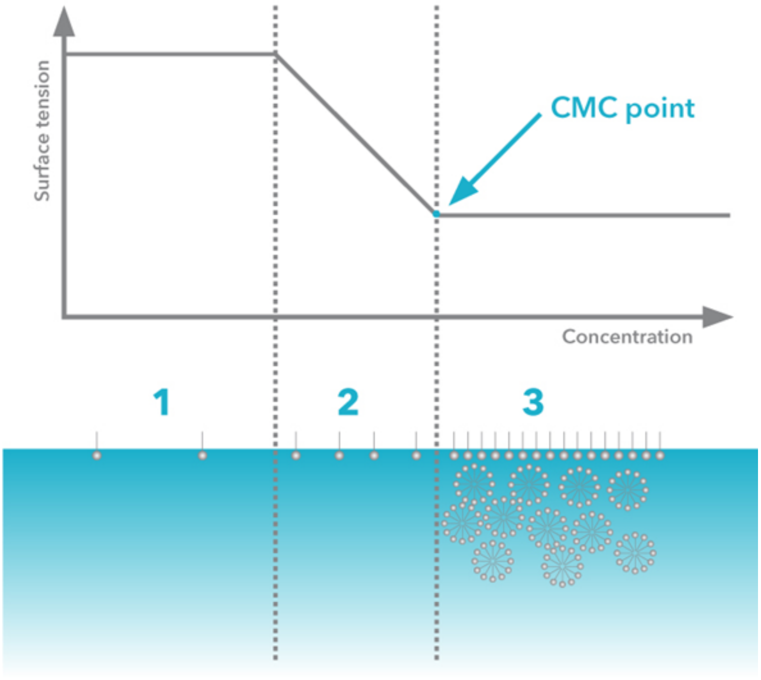
[2] R. Blossey, "Self-cleaning surfaces - virtual realities", Nature Materials 2 (2003) 301.

12.4 Critical micelle concentration

Surfactants are compounds that lower the surface tension of the liquid, the interfacial tension between two liquids or interfacial tension between a liquid and solid. Surfactants can act as detergents, wetting agents, emulsifiers, foaming agents and dispersants. Surfactants are amphiphilic molecules that contain the hydrophobic hydrocarbon tail and hydrophilic head. Therefore, surfactant molecule contains both a water soluble and water insoluble (or oil soluble) component (Figure A). When these molecules are on air-water or oil-water interfaces they align so that the hydrophilic part is in water phase and hydrophobic part in air (or oil) phase (Figure B). Another energetically favorable form for the surfactant molecules in water solution are micelles where the hydrophobic tails are protected by the hydrophilic head groups (Figure C).



In colloidal and surface chemistry, the critical micelle concentration (CMC) is defined as the concentration above which micelles form. At low surfactant concentration the surfactant molecules arrange on the surface. When more surfactant is added the surface tension of the solution starts to rapidly decrease since more and more surfactant molecules will be on the surface. When the surface becomes saturated, the addition of the surfactant molecules will lead to formation of micelles. This concentration point is called critical micelle concentration. A graph of surface tension vs. logarithm of surfactant concentration will look like in Figure below.



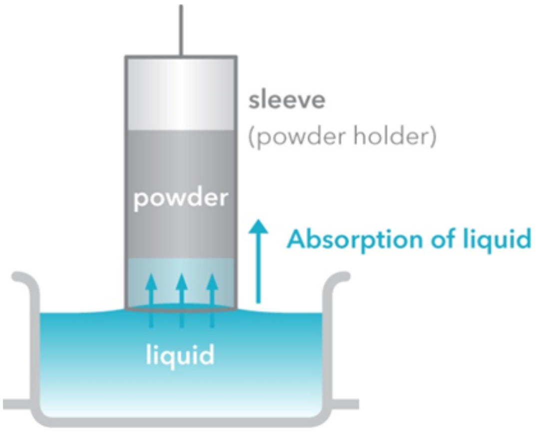
Three different phases can be identified;

1. At very low surfactant concentration only slight change in surface tension is detected.
2. Addition of surfactant decreases the surface tension drastically
3. At CMC point, surface becomes saturated and the addition of surfactant molecules don't effect on the surface tension.

12.5 Powder wettability

Direct contact angle measurements have become a standard experiment when dealing with planar solid surfaces or cylindrical materials, like fibers. Such direct approaches cannot be used on finely dispersed solid materials, like powders. Usual investigation methods include (1) contact angle measurement on tablets by using sessile drop and (2) capillary rise or Washburn method.

Capillary rise or Washburn method can be done by using force tensiometer and a special type of powder holder. The measurement set up is shown in figure below. The powder holder, with small holes in the bottom, is immersed into the liquid and the amount of liquid absorbed into the powder bed is measured against time.



Capillary rise method is based on the Poiseuille law related to the liquid flow through a capillary

$$v = \frac{R_D^2 \Delta P}{8\eta \ l} \qquad [1]$$

where v is the kinetics of flow, R_D the mean hydrodynamic radius of the capillary, η the viscosity of the liquid, l the length of the capillary and ΔP the pressure difference. ΔP can be expressed as a sum of a capillary pressure and a hydrostatic pressure. Thus equation [1] can be written

$$\frac{dh}{dt} = \frac{R_D^2}{8\eta h}\left[\frac{2\gamma_l cos\theta}{R_S} \pm \rho g h\right] \qquad [2]$$

h is the liquid front height, g the gravitational constant, R_S the mean static radius of the capillary, and ρ the liquid density. Now if hydrostatic pressure is neglected and we suppose that $r = R_D^2/R_S$, integration of the equation [2] with boundary condition h=0 when t=0 gives

$$h^2 = \frac{r\gamma_l cos\theta}{2\eta}t \qquad [3]$$

Equation [3] is called Washburn equation. The porous bed is considered as a bundle of parallel capillaries of constant radius. The use of this equation would require a visual observation of the moving liquid front. Since this is much more difficult to do than measuring the gained weight, the weight w is related to the height in the cylinder by

$$w = \varepsilon\rho\pi R^2 h \qquad [4]$$

where ε is the porosity of the packed powder column, ρ the density of the liquid, and R the inner radius of the tube. And finally combining the equations [3] and [4]

$$w^2 = \left(r\varepsilon^2(\pi R^2)^2\right)\frac{\rho^2\gamma_l cos\theta}{2\eta}t \qquad [5]$$

which leads to

$$w^2 = c\,\frac{\rho^2\gamma_l cos\theta}{2\eta}t \qquad [6]$$

Equation [6] is often referred as modified Washburn equation. The term c is a geometric factor and is constant as long as packing and the particle size remains similar. It has to be experimentally determined to each type of packing and powder combination. Precise and accurate determination of the constant c is critical for the correct application of the Washburn equation. In practice, to solve the material constant the measurement has to be done first with the completely wetting liquid such as hexane, heptane or octane. The contact angle can thus be assumed to be zero (cos0 =1) and the material constant c can be calculated if the properties of the liquid are known. After definition of the material constant the contact angle measurement with the liquid of interested can be done. A powder packing method has to be repeatable and carefully controlled since it is not possible to measure the material constant and then re-use the same powder for actual contact angle measurement.

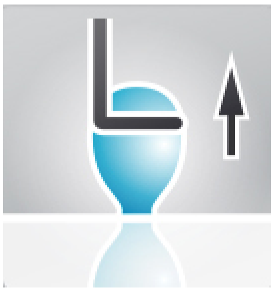
12.6 Adhesion Force

Adhesion force characterizes the force that is required to detach a liquid droplet from a surface that it contacts. It provides a way to quantify the attractive interaction between liquid and solid.

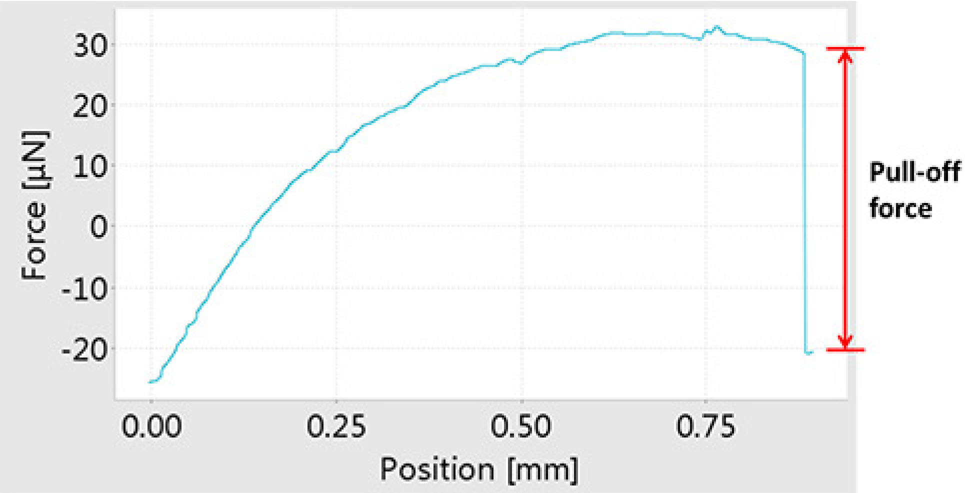
The adhesion force of a surface to liquid depends on surface wettability of the surface, the volume of liquid droplet, liquid surface tension, and the measuring procedure employed. At given measuring conditions (i.e. fixed liquid volume and measuring procedure), the adhesion force is determined by contact angle of the surface; more specifically, by the receding contact angle of the surface. Receding contact angle is the critical contact angle below which the solid-liquid-gas contact line retraction is initiated. A surface with larger receding contact angle exhibits lower adhesion force.

Measurement of adhesion force

The measuring method of adhesion force is schematically shown in below. A liquid droplet attached to a micro-balance is first made to contact with the sample surface, and then is separated slowly from it. During this process, the force-displacement curve is recorded by the micro-balance. The adhesion force is measured as the pull-off force when separating the surface and the droplet. The next figure shows a typical force-displacement curve obtained from a hydrophobic surface. The adhesion force between the surface and a water droplet is shown as the pull-off force.



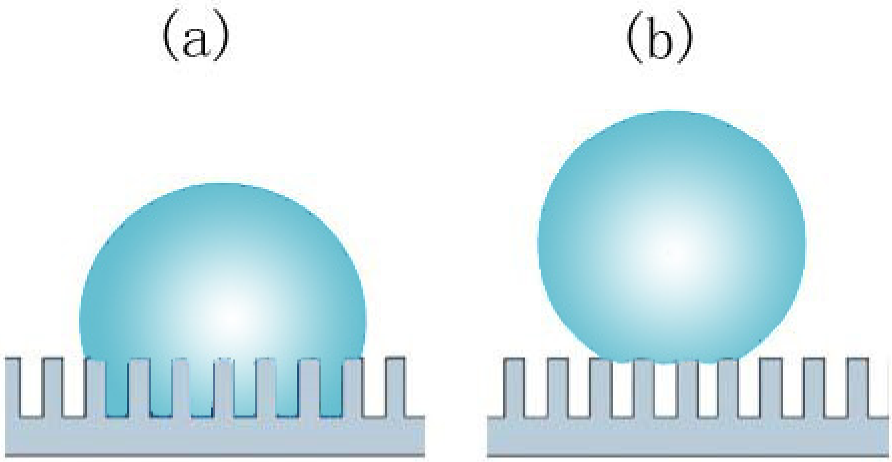
Experimental setup for measuring the adhesion force.



Force-displacement curve obtained from a hydrophobic surface and a water droplet. The red arrow indicates the pull-off force.

Applications

Adhesion force can be used to characterize liquid repellency of self-cleaning surfaces as surfaces with low solid-liquid adhesion force are more suitable for self-cleaning applications. It can also give information on the wetting states of micro-textured surfaces that exhibit large apparent contact angles. For example, a surface in Wenzel type wetting state (a) usually shows large adhesion force whereas a surface in Cassie-Baxter state (b) is expected to exhibit much lower values



Two different wetting states. (a) Wenzel state, and (b) Cassie-Baxter state.

13 Technical specifications

Sigma 700	Extended range microbalance
Maximum load	210 g
Weighing resolution*	0.01 mg
Force resolution	0.1 μN
ST Measuring range	1-2000 mN/m
ST Resolution with standard probe**	0.001 mN/m
Contact angle range	0-180 °
Contact angle resolution	0.01 °
Taring	Automatic computer controlled taring
Calibration and locking	Automatic

Sigma 701	Torsion wire electrobalance
Maximum load (701)	5 g
Weighing resolution*	0.005 mg
Force resolution	0.05 μN
ST Measuring range	1-2000 mN/m
ST Resolution with standard probe**	0.001 mN/m
Contact angle range	0-180 °
Contact angle resolution	0.01 °
Taring	Manual
Calibration and locking	Manual

* Actual resolution of balance.

** Resolution in mN/m or dynes/cm depends on accuracy of balance and length measurement of the Du Nouy ring or Wilhelmy plate. Resolutions given above are theoretical limits for standard Attension probes made according to the requirements of DIN and ASTM standards. In actual practice reproducibility of surface and probe will limit the reproducibility of data to about 0.01 mN/m.

Lifting System

Stage Speed	0.01 - 500 mm/min
Stage position resolution	0.016 µm
Maximum stroke	70 mm

Computer interface

Connection	USB (RS232 as option)

Voltage and current

Input voltage	100 – 240 Vac
Frequency	50 – 60 Hz
Input current (Sigma 700)	100 – 220 mA
Input current (Sigma 701)	100 – 180 mA
Fuses	T1.0A 5x20 mm

Computer requirements

PC running Windows 10 (32 or 64 bit), Windows 8 (32 or 64 bit) or Windows 7 (32 or 64 bit)

1 GHz processor (the larger the better)

1GB MB RAM memory (the more the better)

40 GB hard disk drive (20 GB free)

1 USB port (additional ports needed with CMC dispensers)

Accessories such as water bath and liquid dispensers may require a free RS-232 port or the use of RS-232 to USB adapters.

Environmental conditions

Ambient temperature	15 – 30 °C
Ambient pressure	700 to 1060 hPa
Ambient humidity	20 – 80% (non-condensing)

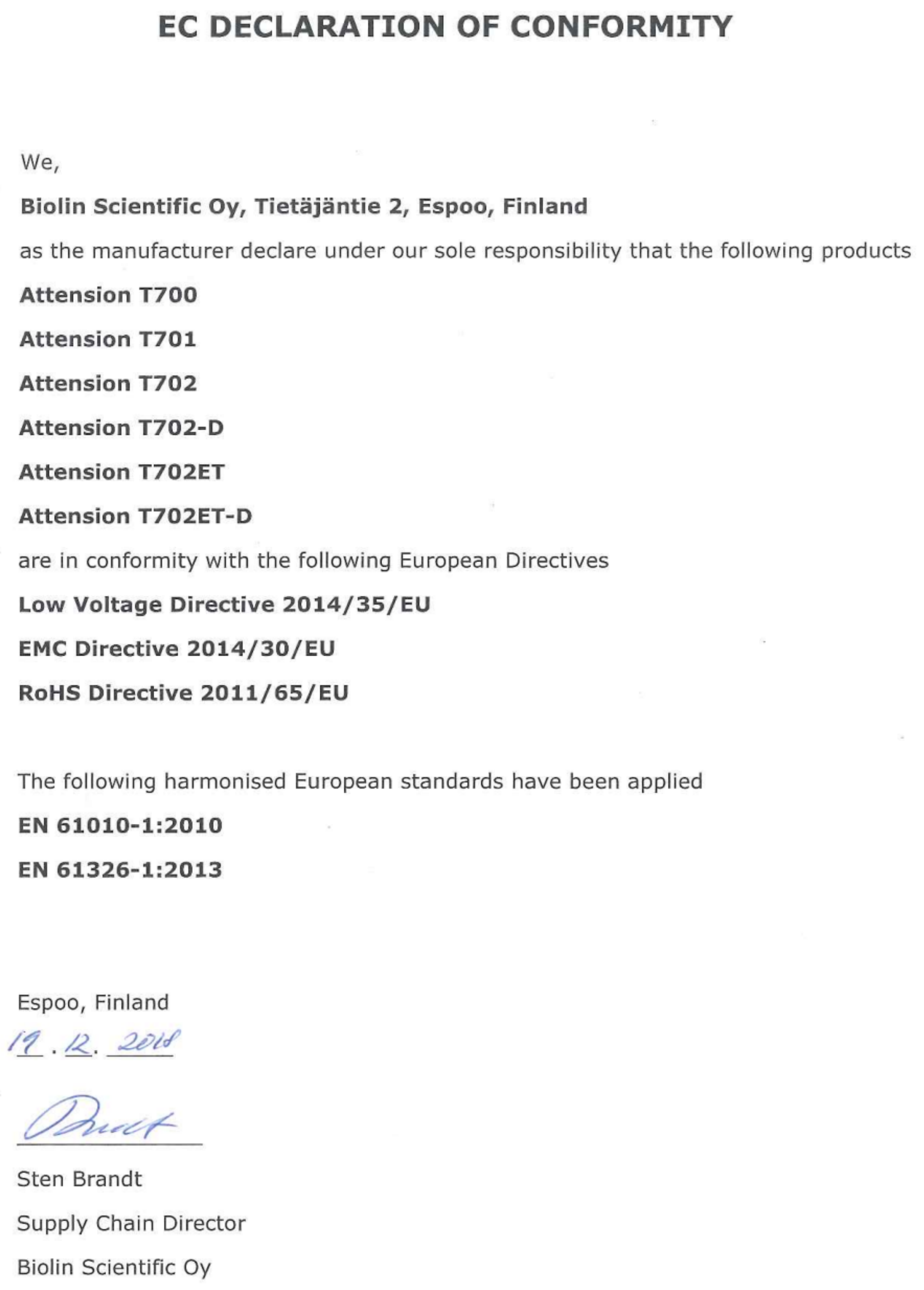
14 Contact and Support

If any problems arise please feel free to contact your local distributor or Biolin Scientific directly.

https://www.biolinscientific.com/contact-us

info@biolinscientific.com

15 EC Declaration of Conformity



EC DECLARATION OF CONFORMITY

We,

Biolin Scientific Oy, Tietäjäntie 2, Espoo, Finland

as the manufacturer declare under our sole responsibility that the following products

Attension T700

Attension T701

Attension T702

Attension T702-D

Attension T702ET

Attension T702ET-D

are in conformity with the following European Directives

Low Voltage Directive 2014/35/EU

EMC Directive 2014/30/EU

RoHS Directive 2011/65/EU

The following harmonised European standards have been applied

EN 61010-1:2010

EN 61326-1:2013

Espoo, Finland
19.12.2018

Sten Brandt
Supply Chain Director
Biolin Scientific Oy