QCM-D viscosity measurement

A quick guide to how to perform a QCM-D viscosity measurement and a step by step manual to viscosity modeling in QTools.

Introduction to viscosity

A **Newtonian** fluid flows like water – its stress versus rate of strain curve is linear and passes through the origin. The constant of proportionality is known as viscosity. In QCM-D measurements, this means that the fluid will have the same viscosity regardless of frequency. This allows for viscosity modelling at multiple overtones which gives more information about the system.

A fluid that does not obey this rule is **non-Newtonian**, i.e. the viscosity changes with the applied strain rate. When using QCM-D, the fluid will have different viscosities at different harmonics. A shear thinning fluid for example, will have a lower viscosity at higher frequencies. Therefore, the result will also be different from other viscometers, measuring under other circumstances.

Viscoelastic materials exhibit both viscous and elastic characteristics when undergoing deformation. Viscoelastic models are used to explain the behaviours of viscoelastic materials. The Maxwell viscoelastic model represents a liquid with some additional reversible (elastic) deformations, whereas the Voigt viscoelastic model resembles a solid undergoing reversible viscoelastic strain. This means that viscoelastic fluids are best represented by the Maxwell viscoelastic model.

QCM-D viscosity measurement and modeling have different approaches depending on the properties of the system. This guide contains two sections: **Section A** is a simple bulk viscosity measurement of a fluid – Newtonian or viscoelastic. **Section B** contains a method that also takes surface adsorption onto the sensor into consideration. Both methods can also be used for non-Newtonian fluids but then modelling can only be done at one overtone at the time.

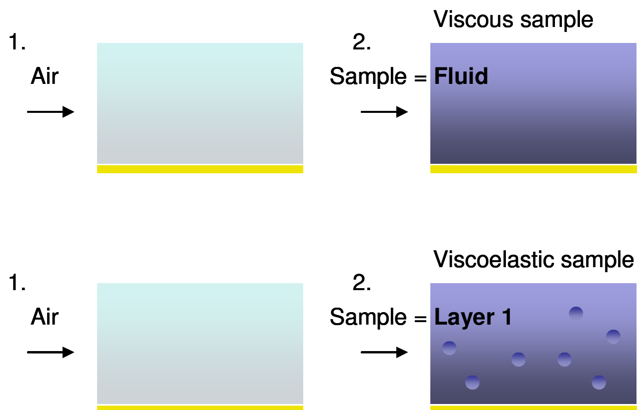
Section A

Simple bulk viscosity measurement

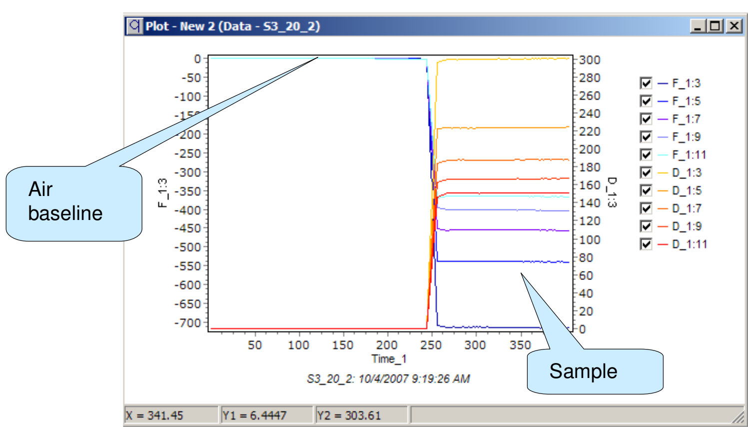
This procedure can be used both for Newtonian and viscoelastic fluids. The adsorption to the sensor surface is assumed to be negligible.

Measurement setup

1. Start the measurement in air and produce a stable base line.
2. Pump the fluid into the measurement chamber. Once the fluid reaches the measurement chamber, let it flow until f and D values stabilizes.
3. To see if there is any flow dependence of the fluid, stop the pump and see if the f and D values change.
4. Stop measurement

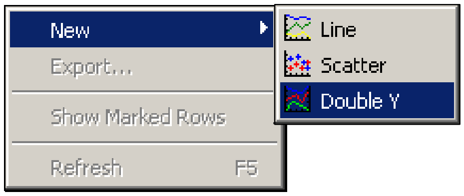


Illustrations of the scenario on the sensor (yellow line).
Bold letters show the names that are used for modeling in QTools.

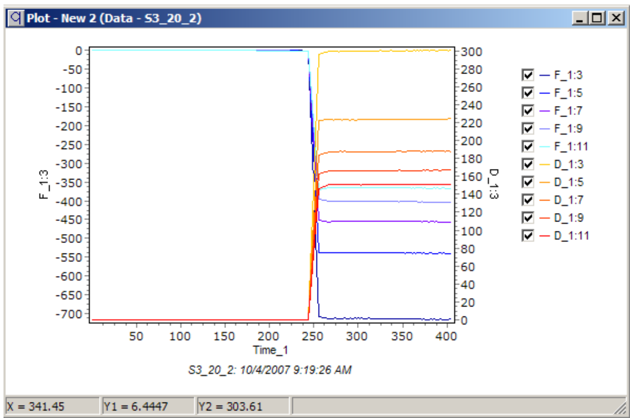


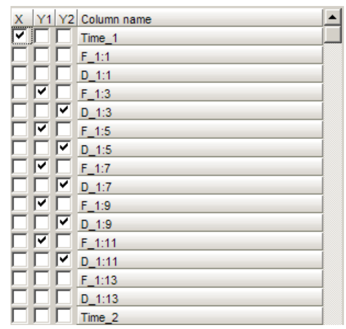
Example of frequency and dissipation shifts during measurment.

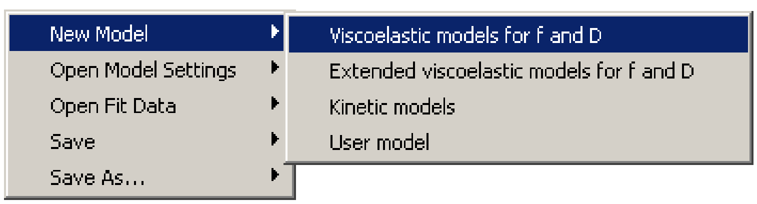
QTools Step by Step (A)



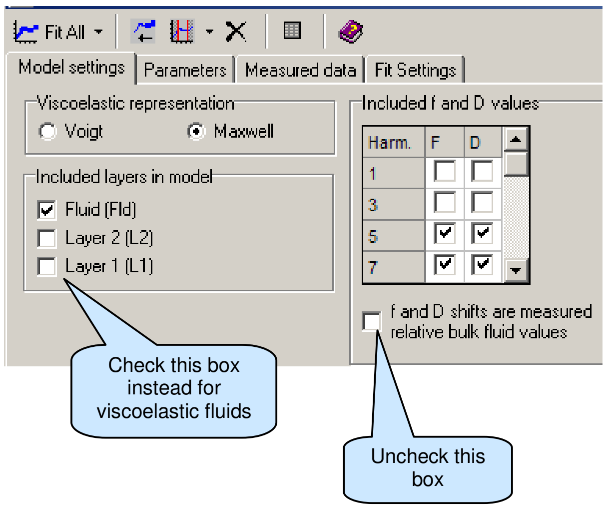
1 For an overview graph of the data-set, open the “Plot” menu and then “New/Double Y”. Check time in X column and f and D values in the Y columns respectively.







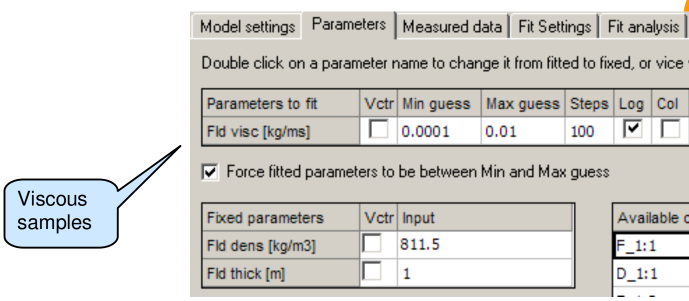
2 Go back to the spreadsheet, and open “Modeling/New Model/Viscoelastic models…”.

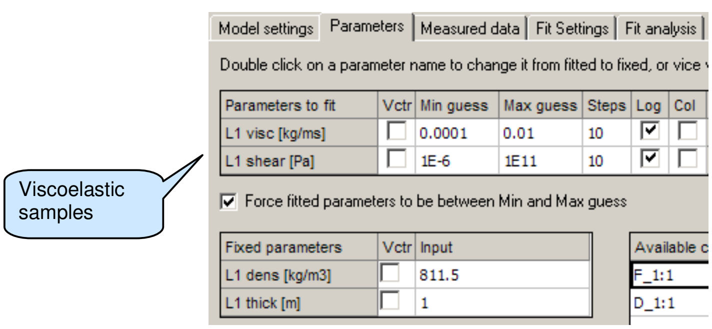


3 In the Modeling Center there are 4 tabs where the fitting process is prepared; start at "**Model settings**":

a) If the fluid is only viscous, check "Fluid".
b) If the fluid is viscoelastic, check "Layer 1" instead. Choose Maxwell viscoelastic model since the fluid is more viscous than elastic.
c) Uncheck "f and D shifts are measured relative bulk fluid values".
d) Set the number of included harmonics – the more the better, however the fundamental tone should normally be disregarded.
e) If you suspect frequency dependence i.e. non-Newtonian behaviour, model one harmonic at a time.

4 Continue with next tab "**Parameters**"

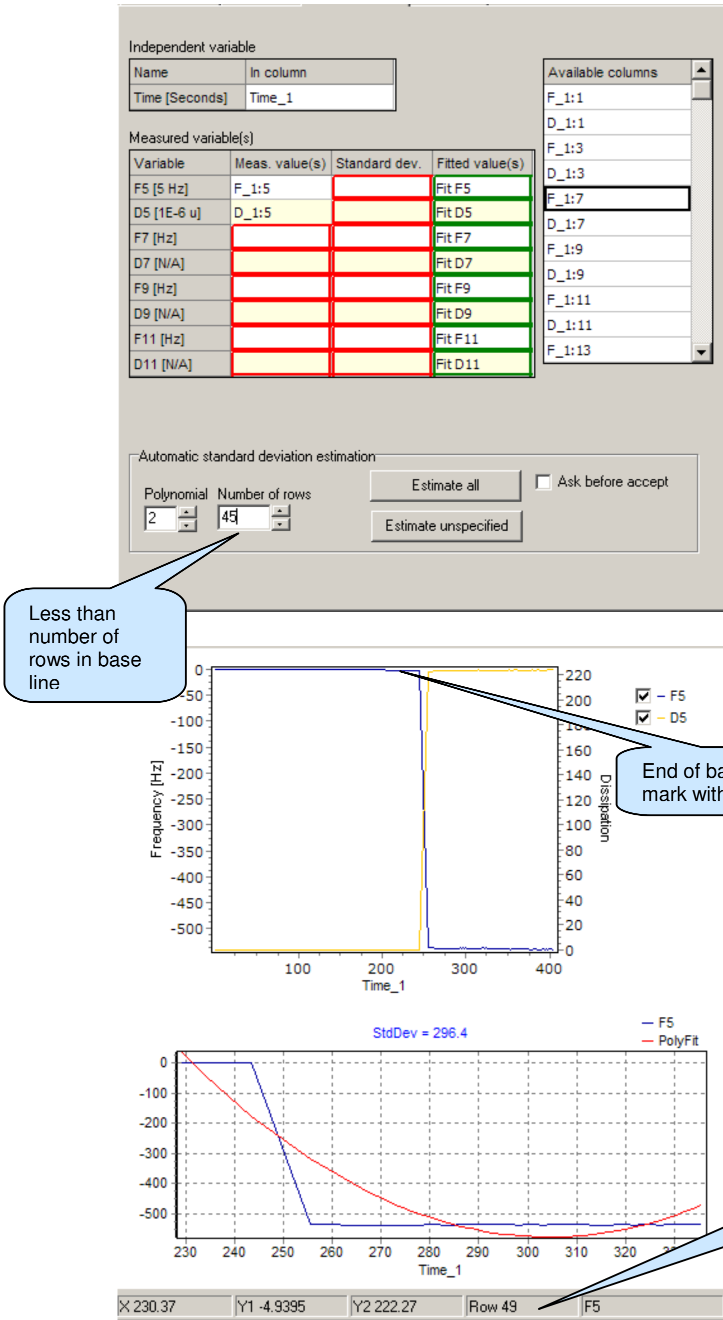




a) Double-click on the "parameter to fit" cells to include/exclude in the modelling. Note that density and viscosity cannot be fitted at the same time (e.g. a 10% increase in density and a simultaneous 10% decrease in viscosity will not change the fit).
b) Set thickness to 1 for infinite thickness.
c) Insert guesses for minimum and maximum possible values for each modelled parameter. These intervals form a grid of coordinates that will be scanned through to find the best starting point for the fitting of the data.
d) Uncheck vector, to achieve a mean value of the viscosity.

Default settings:

- Let "Vctr" be ticked if you want to have the output as a column (vector) and not only one value for the whole data set. An output column will automatically be added to the spreadsheet.
- "Steps" = 10. More steps will make the initial scan for the best starting point more detailed.



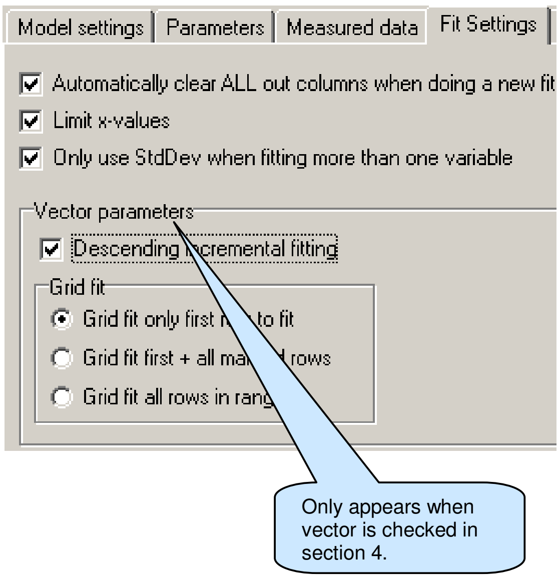
5 Continue with next tab "**Measured data**".

a) Drag and drop the F and D columns from the flow module of interest, found under "Available Columns"; place under "Meas. value(s)". The chosen curves will appear in a graph to the right. Check that the "Fitted value(s)" column gets the right names.

b) Click "Estimate all" to get the standard deviation for each curve. Choose number of rows less than number of rows included in the base line to get a low standard deviation.

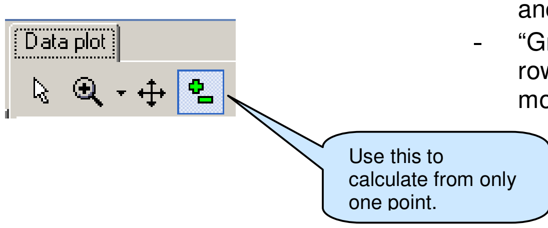
Default settings:

- "Independent variable" = x-axis variable, usually time.
  Standard deviation settings = 2:nd degree of polynomial and 100 rows included in calculations.



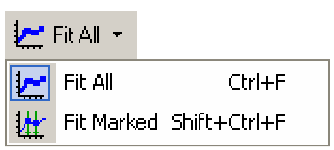
6 Continue with next tab "**Fit settings**".

a) Click "Limit x-values"; two red curtains will appear that can be slid along the x-axis. Slide the left curtain to include only the data for the fluid,
or click the green + - button and mark one representative point on the curve.



Default settings:

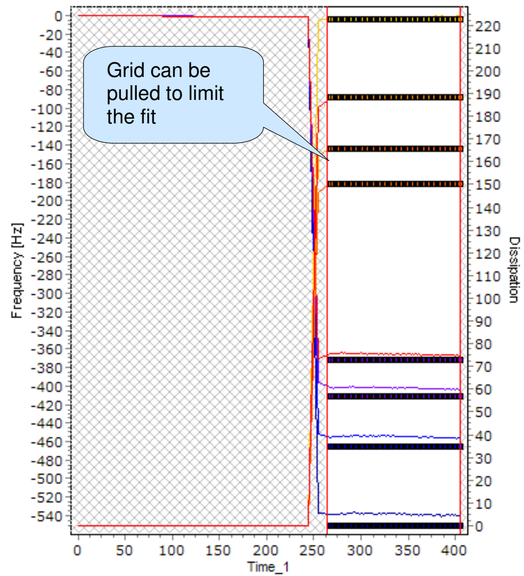
- "Automatically clear ALL out columns..." checked
- "Only use StdDev when fitting more than one variable" checked.
- "Descending incremental fitting" checked – means that the fitting is performed backwards. This is standard when the measurement starts with nothing or almost nothing on the surface and mass is added over time.
- "Grid fit only first row to fit" checked. The more rows that are included in the initial grid scan, the more calculations (=time) is needed.

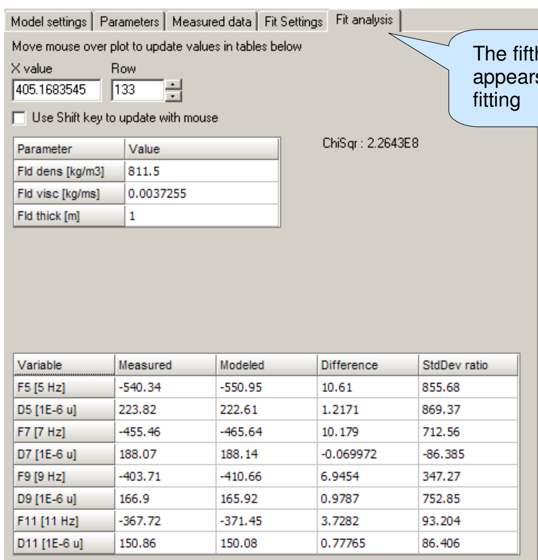


7 Click "**Fit All**" to start the fitting calculations.

Or click "**Fit marked**" if the green + - marker was used.

If the fit menu is greyed, there is information missing in any of the cells (marked in red).





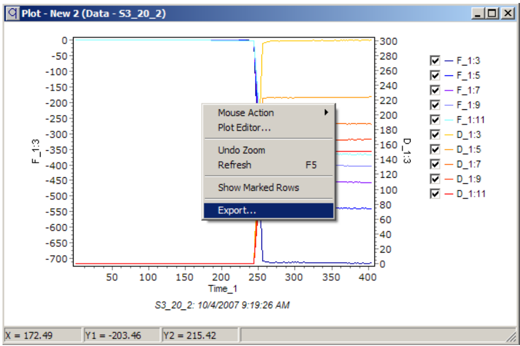
8 In the graph, the fitted values will now appear as boxed curves.

A fifth tab will also appear, with detailed fitting results. Here the calculated viscosity value will appear.

The fit of the model is shown underneath. Here you can see how close the modeled f and D values are to the measured values.

If the fit is not satisfying, the following changes in settings may **improve the results**:

a) Un-check “Force fitted parameters…” under Parameter’s tab.
b) Change min. and max. guesses to create a new starting grid.
c) Exclude overtones that show different behavior than the others (and therefore may be less trusted).
d) Change values of fixed parameters.
e) Try to model one overtone at a time. If the viscosity decreases/increases with frequency, there is a frequency dependence and the fluid is non-Newtonian.



9

Storing of data:

- QTools data spreadsheets can be saved as "*.qtd" files.
- Plots can be saved as "*.qtp" files.
- Model settings can be saved as "*.qms" files.
- Graphs can be exported as picture format files, via the plot right-button menu.

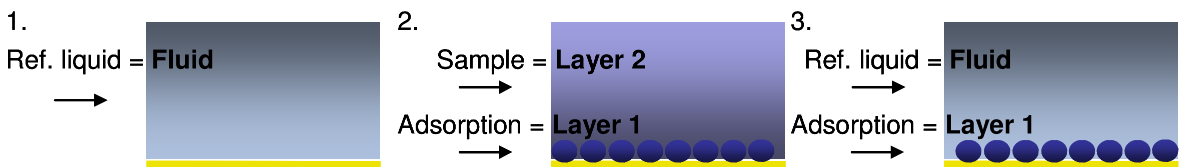
Section B

Bulk viscosity measurement with surface adsorption

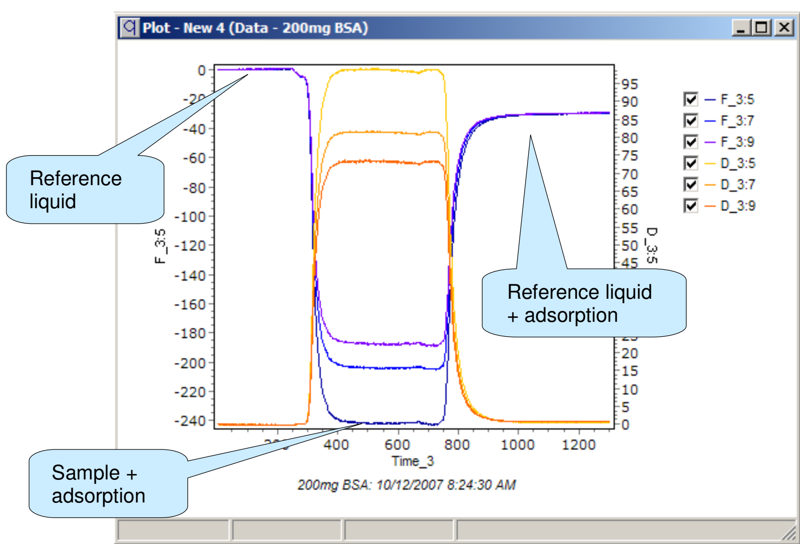
This procedure can be used both for viscous and viscoelastic samples with surface adsorption to the sensor. It could also be used to prove that surface adsorption is negligable.

Measurement setup

1. Start the measurement in a reference liquid with known viscosity and density (for example water) and produce a stable base line.
2. Exchange to sample fluid and wait until f and D-values stabilizes.
3. Exchange again to the reference liquid.
4. Stop measurement.

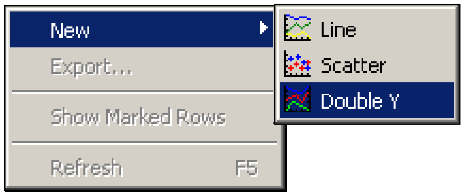


Illustrations of what is happening on the sensor (yellow line).
Bold letters show the names that are used for modeling in QTools.

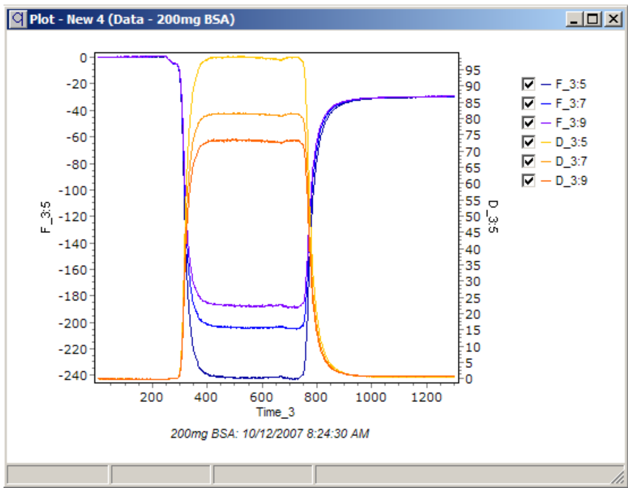


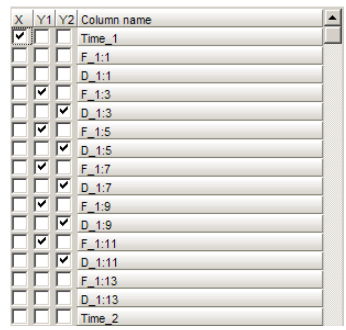
Example of frequency and dissipation shifts during a measurement.

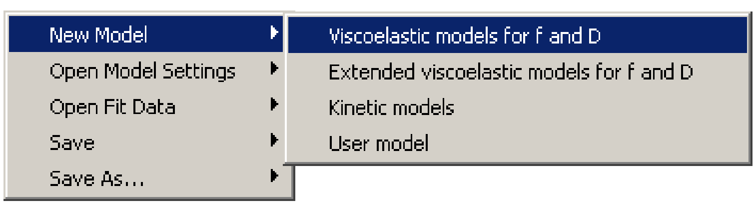
QTools Step by Step (B)



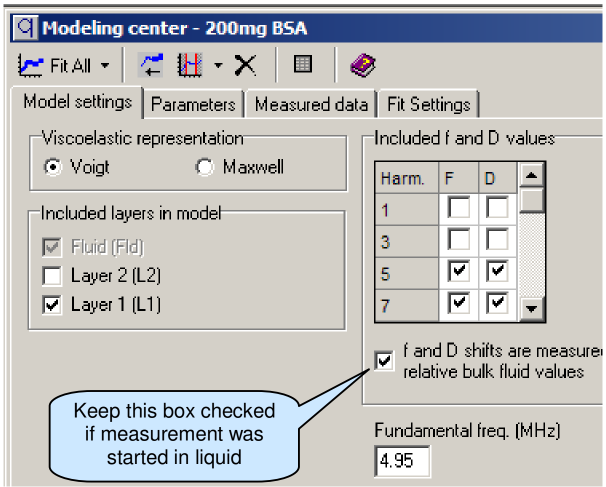
1 For an overview graph of the data-set, open the “Plot” menu and then “New/Double Y”. Check time in X column and f and D values in the Y columns respectively.





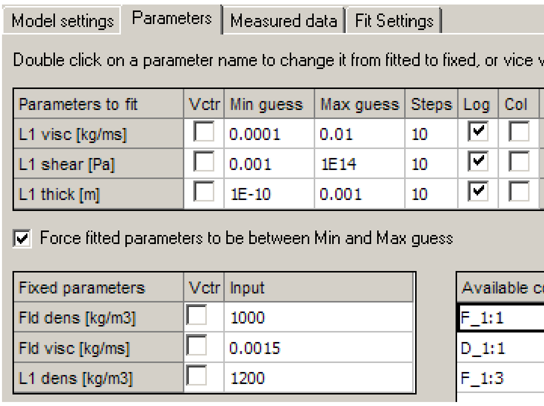


2 Go back to the spreadsheet, and open “Modeling/New Model/Viscoelastic models…”.



3 In the Modeling Center there are 4 tabs where the fitting process is prepared; start at "**Model settings**":

a) Start to model the surface adsorption.
b) Choose **Voigt** viscoelastic model since the adsorbed layer is fairly rigid.
c) "Fluid" will refer to the reference liquid and has to have known viscosity and density. "Layer 1" will be the adsorbed layer.
d) Set the number of included harmonics – the more the better. However the fundamental tone should normally be disregarded. **This step requires modelling at multiple overtones**.

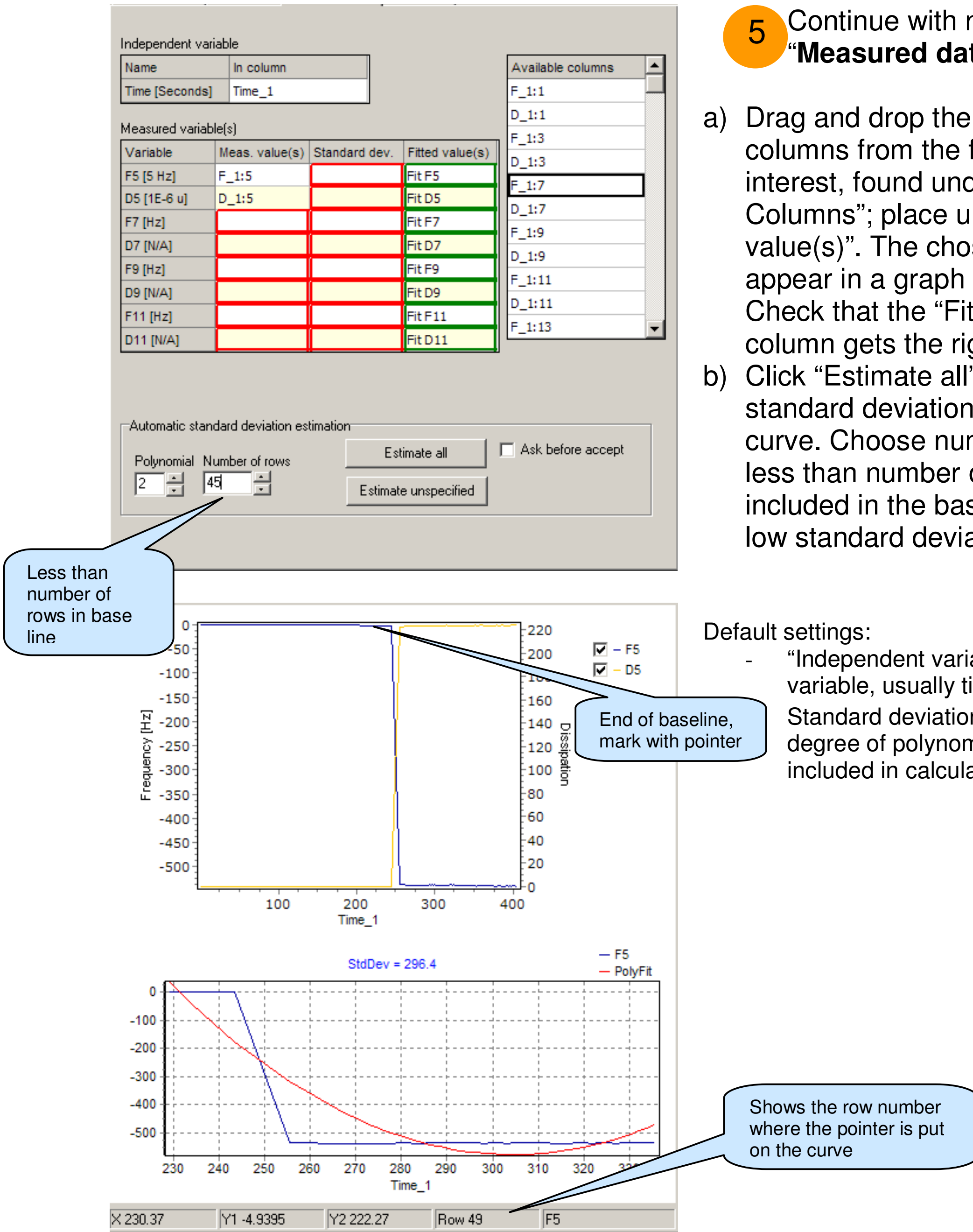


Default settings:

- Let "Vctr" be ticked if you want to have the output as a column (vector) and not only one value for the whole data set. An output column will automatically be added to the spreadsheet.
- "Steps" = 10. More steps will make the initial scan for the best starting point more detailed

4 Continue with next tab "**Parameters**".

a) Double-click on the "parameters to fit" cells to include/exclude in the modelling. Note that density and viscosity cannot be fitted at the same time (e.g. a 10% increase in density and a simultaneous 10% decrease in viscosity will not change the fit).
b) Fluid parameters will be the known values for the reference liquid.
c) Estimate a density of the adsorbed layer. It will be compensated by the layer thickness.
d) Insert guesses for minimum and maximum possible values for each modelled parameter. These intervals form a grid of coordinates that will be scanned through to find the best starting point for the fitting of the data.
e) Uncheck vector, to get mean values for the adsorbed layer.



5 Continue with next tab "**Measured data**".

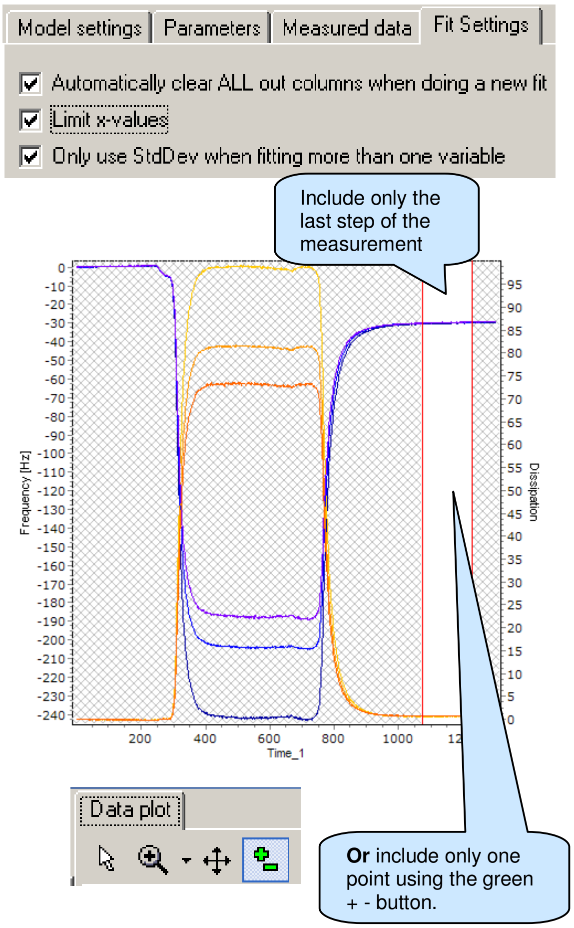
a) Drag and drop the F and D columns from the flow module of interest, found under "Available Columns"; place under "Meas. value(s)". The chosen curves will appear in a graph to the right. Check that the "Fitted value(s)" column gets the right names.

b) Click "Estimate all" to get the standard deviation for each curve. Choose number of rows less than number of rows included in the base line to get a low standard deviation.

Default settings:

- "Independent variable" = x-axis variable, usually time.

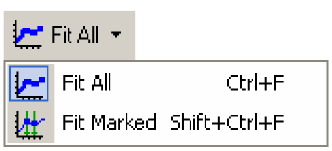
  Standard deviation settings = 2:nd degree of polynomial and 100 rows included in calculations.



6 Continue with next tab “**Fit settings**”.

a) Click “Limit x-values”. Two red curtains will appear that can be slid along the x-axis.
b) Slide the left curtain to include only the data for the surface adsorption + reference liquid.
c) OR click the green + - button and mark only one representative point.

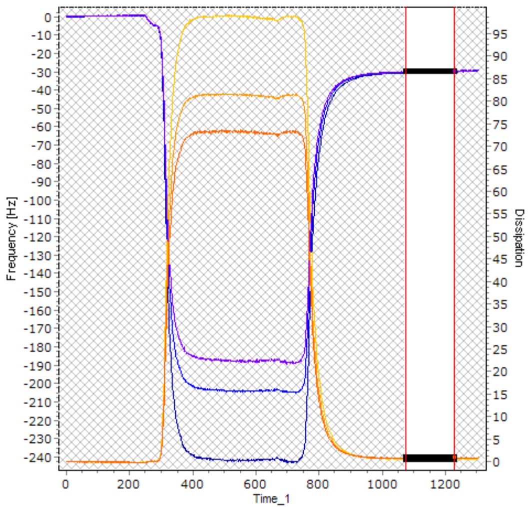
Default settings:
- “Automatically clear ALL out columns...” checked
- “Only use StdDev when fitting more than one variable” checked.
- “Descending incremental fitting” checked – means that the fitting is performed backwards. This is standard when the measurement starts with nothing or almost nothing on the surface and mass is added over time.
- “Grid fit only first row to fit” checked. The more rows that are included in the initial grid scan, the more calculations (=time) is needed.



7 Click “**Fit All**” to start the fitting calculations.

Or click “**Fit Marked**” if the green + - button was used.

If the fit menu is greyed, there is information missing in any of the cells (marked in red).

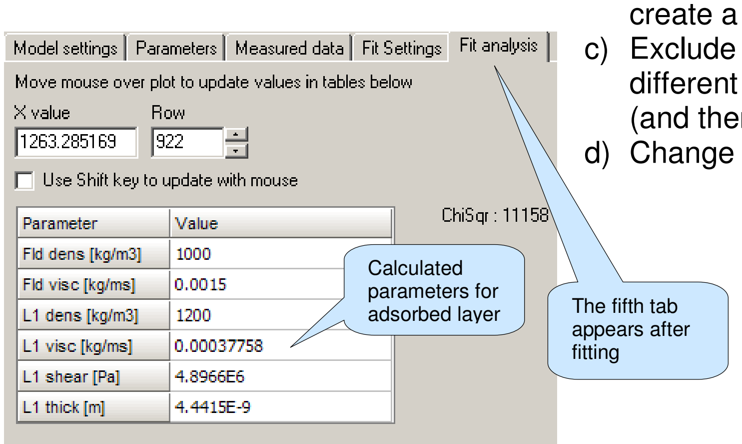


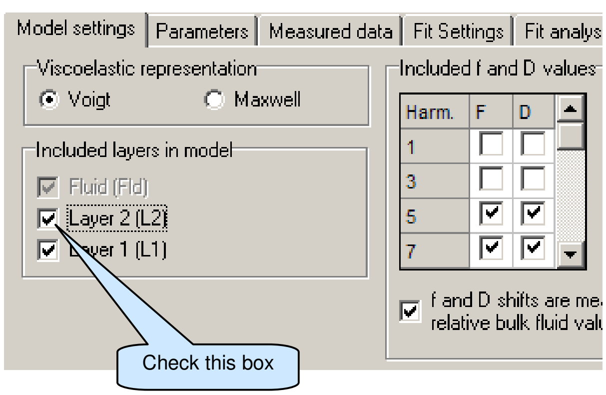
8 In the graph, the fitted values will now appear as boxed curves.

A fifth tab, “Fit analysis”, will also appear, with detailed fitting results. Here the calculated parameters for the adsorbed layer will appear.

If the fit is not satisfying, the following changes in settings may **improve the results**:

a) Un-check “Force fitted parameters…” under Parameter’s tab.
b) Change min. and max. guesses to create a new starting grid.
c) Exclude overtones that show different behavior than the others (and therefore may be less trusted).
d) Change values of fixed parameters.

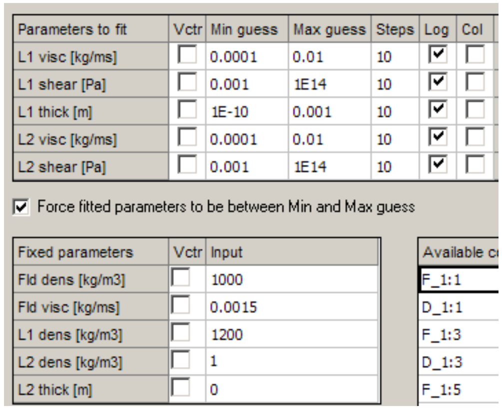




9 Go back to “**Model settings**”:

a) Add Layer 2, this will be the layer for the sample fluid. (See pictures under Measurement setup.)

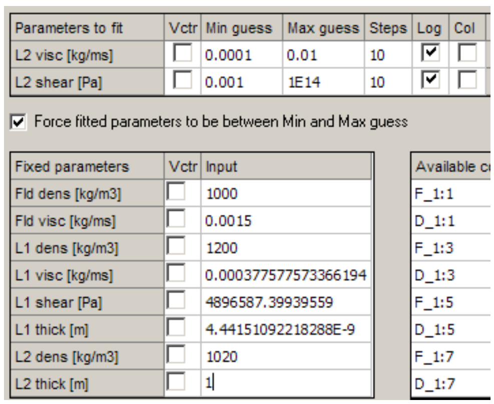
The window will appear like this

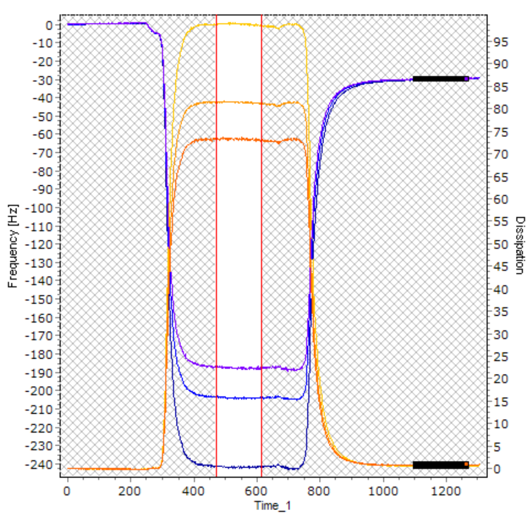


10 Continue with next tab "**Parameters**".

a) Double-click on the L1 parameter cells to move them to fixed parameters. They will get the values from the previous fit automatically.
b) Set the density for the sample fluid.
c) Set the Layer 2 thickness to 1 for infinite thickness.
d) Insert guesses for minimum and maximum possible values for each modelled parameter.
e) Uncheck vector, to get a mean value of the viscosity.

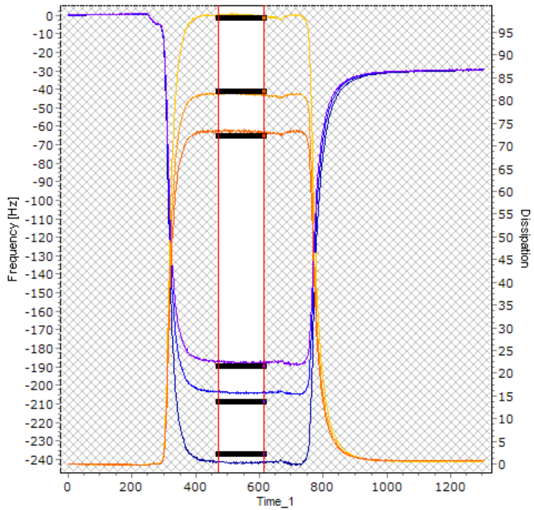
Move L1 parameters here





11 Move grid to model the part where the fluid is measured.

Or move the green line if + - button was used.



Parameter	Value
Fld dens [kg/m3]	1000
Fld visc [kg/ms]	0.0015
L1 dens [kg/m3]	1200
L1 visc [kg/ms]	0.00037758
L1 shear [Pa]	4.8966E6
L1 thick [m]	4.4415E-9
L2 dens [kg/m3]	1020
L2 visc [kg/ms]	0.0036518

Modeled viscosity for the sample

Variable	Measured	Modeled	Difference	StdDev ratio
F5 [5 Hz]	-241.72	-237.02	-4.6986	-78.05
D5 [1E-6 u]	98.318	98.191	0.12733	4.9935
F7 [7 Hz]	-204.08	-208.76	4.6868	85.659
D7 [1E-6 u]	81.236	82.044	-0.80794	-39.22
F9 [9 Hz]	-187.3	-189.51	2.2018	26.706
D9 [1E-6 u]	72.901	72.268	0.63293	21.825

12 Click “**Fit All**” / “**Fit Marked**” to start the fitting calculations. If the fit menu is greyed, there is information missing in any of the cells (marked in red).

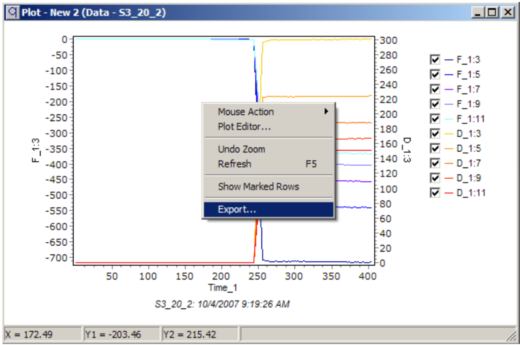
In the graph, the fitted values will now appear as boxed curves.

The modeled viscosity for the fluid will be found as “L2 visc” under “Fit analysis”.

Underneath, the fit of the model is shown. Here you can see how close the modeled f and D values are to the measured values.

If the fit is not satisfying, the following changes in settings may **improve the results**:

a) Un-check “Force fitted parameters…” under Parameter’s tab.
b) Change min. and max. guesses to create a new starting grid.
c) Exclude overtones that show different behavior than the others (and therefore may be less trusted).
d) Change values of fixed parameters.
e) Try to model one overtone at a time. If the viscosity decreases/increases with frequency, there is a frequency dependence and the fluid is non-Newtonian. **Can only be done from step 9.**
f) Exclude Layer 1, many times it can be assumed to have negligable impact on the result.



13 Storing of data:

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- Plots can be saved as "*.qtp" files.
- Model settings can be saved as "*.qms" files.
- Graphs can be exported as picture format files, via the plot right-button menu.