Maximum Bubble Pressure Tensiometer MPT 2

LAUDA

BUBBLE PRESSURE TENSIOMETER
MPT 2
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Operating Instructions for the Maximum Pressure Tensiometer MPT 2

I. Introduction

These Operating Instructions should enable you to achieve the optimum use of the many facilities of the LAUDA Maximum Pressure Tensiometer MPT 2.

In view of the complexity of this software it is not possible, despite taking every care, to exclude minor errors in operation. In this case you are asked to advise us as soon as possible so that such errors can be immediately corrected. Please contact us at the address below, giving full details of your observations and including your complete address as well as the invoice and delivery note numbers.

Please note the SOFTWARE LICENCE AGREEMENT and the SOFTWARE LICENCE CARD which are given below. In accordance with our software policy we make every effort to provide our customers with the best current software version. In order for existing users to benefit from these updates we require the details shown in the SOFTWARE LICENCE CARD. In addition we are able after receipt of this card to provide technical support and undertake any warranty action required.

Please address your suggestions and criticisms to:
LAUDA DR. R.WOBSER GmbH & CO.KG
Instrument Department
P.O. Box 1251
D-97912 Lauda-Königshofen
Germany

I.1 LAUDA Software Licence Agreement

LAUDA software (called "Licence Software" below) has to be used under the following conditions:

1. With the first use or the first loading of the Licence Software supplied the user recognises the following points.
2. Any legal or warranty claim can only be made following timely despatch of the SOFTWARE LICENCE CARD. Timely is taken as receipt of the SOFTWARE LICENCE CARD by LAUDA within 4 weeks after purchase of the Licence Software.
3. If you do not agree with the conditions listed here you must immediately return the product to LAUDA, together with a copy of the invoice and of the delivery note, for the refund of the purchase price.
4. You are entitled to use this Licence Software on any compatible computer provided that this Licence Software is only used on a single computer and by a single person, and that you are in possession of the original cassette or original diskette
5. You are entitled to modify this Licence Software according to your own requirements. The legal and warranty entitlement listed under Item 2, as well as any technical support from LAUDA, do however apply and are given exclusively for the ORIGINAL VERSION and to any special versions prepared by LAUDA.
6. You are entitled to make copies of this Licence Software and of these Operating Instructions.
7. You are not entitled to distribute, hire out or sub-license this Licence Software. This applies to the Licence Software and the Operating Instructions as a whole and also to parts and extracts of it.
8. LAUDA warrants that at the time of delivery the cassettes or diskettes are free from material and manufacturing faults, that the program is stored correctly and completely, and that this Licence Software operates in accordance with the Operating Instructions.
Maximum Bubble Pressure Tensiometer MPT 2

9. LAUDA accepts no liability that this Licence Software is suitable for the task intended by the customer.
10. Lauda accepts no liability for any damage which may be caused by the application of this Licence Software.
11. If one of the conditions contained in this Agreement or a part of it, should be invalid for legal reasons, it is considered as being omitted.

<table>
<thead>
<tr>
<th>SOFTWARE LICENCE CARD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order number of software :........................................</td>
</tr>
<tr>
<td>Purchase date :.......................................................</td>
</tr>
<tr>
<td>Organisation :..................................................................</td>
</tr>
<tr>
<td>User :...............................................................................</td>
</tr>
<tr>
<td>Department :.........................................................</td>
</tr>
<tr>
<td>Building :........................................................</td>
</tr>
<tr>
<td>Address/P.O. Box :................................................................</td>
</tr>
<tr>
<td>Town/Country :.........................................................</td>
</tr>
<tr>
<td>Post Code :.........................................................</td>
</tr>
</tbody>
</table>

This licence card must be completed in full and returned to the following address:
LAUDA DR.R.WOBSER GmbH & CO.KG, Instrument Dept., P.O. Box 1251, 97912 Lauda-Königshofen, Germany

II Description of the Operating Principle

II.1 Applications of the Maximum Pressure Tensiometer MPT 2

The maximum pressure tensiometer MPT 2 measures the dynamic surface tension of liquids. The test samples can be both aqueous solutions of surfactant substances as well as any liquids containing dissolved substances. The result of the measurement is the surface tension as a function of the surface life time.

II.2 Measuring principle

In the maximum pressure tensiometer air is blown through a narrow capillary into the liquid whose surface tension is to be measured. The pressure at the inlet to the capillary, the volumetric flow of air through the capillary, and the time required for bubble formation are measured.

The plot of the pressure P in the instrument gas volume against the volumetric air flowrate L through the capillary shows a significant change in the slope at a special flowrate (Fig. 2.1). The linear range with the steepest slope which occurs at large flowrates L, corresponds to the so-called jet range. In this range there is a laminar air flow through the capillary according to the Hagen-Poiseuille Law. The magnitude of the flowrate is measured by the differential pressure across the capillary. At smaller flowrates there is, depending on the test liquid, a clear deviation from the constant slope of the curve in the linear range. This range of the graph is called the bubble range.
Maximum Bubble Pressure Tensiometer MPT 2

Fig. 2.1: Pressure P in the instrument as a function of volumetric flowrate L

In the bubble range the pressure at the capillary outlet where the bubble is formed, rises (at constant pressure $P_1$ at the capillary inlet) from an initial value $P_2$ to a maximum value $P_1$, and then rapidly falls again to the initial value $P_2$ (Fig. 2.2). The maximum value $P_1$ occurs when the radius $r$ of the bubble at the capillary outlet is equal to the capillary radius $r_{\text{cap}}$ (Fig. 2.3). The pressure is a minimum when the bubble at the capillary outlet bursts and a fresh bubble begins to form. The maximum value $P_1$ of the bubble pressure is used to calculate the surface tension of the test liquid for the particular life of the bubble surface.

Fig. 2.2: Variation of system pressure P as a function of time t, $t_i$ - surface lifetime, $t_b$ - bubble lifetime, $t_d$ - deadtime

The time interval from the start of bubble formation up to the moment where the bubble has the same radius $r$ as the capillary (hemispherical size) is called the surface lifetime $t_i$ (Fig. 2.3). The time $t_d$ required to blow up the bubble from a hemisphere until it detaches is called the deadtime. The
deadtime is calculated by the instrument software from the transition point between the jet and the bubble ranges (Fig. 2.1). The bubble life $t_b$ minus the deadtime $t_d$ gives the surface lifetime $t_l$.

![Diagram](image1)

**Fig. 2.3:** Formation of the bubble at the capillary tip, $R$ – bubble radius in the moment of detachment, $r_o$ – initial bubble radius, $2 r_{cap}$ - diameter of the capillary

![Diagram](image2)

**Fig. 2.4:** Details of the capillary: 1 - capillary, 2 - rejection area

The deadtime $t_d$ is determined by the geometric dimensions of the capillary and bubble. In the maximum pressure tensiometer MPT 2 the special form of the capillary limits the growth of the bubble so that the deadtime $t_d$ can be calculated reliably (cf. Fig. 2.4). The bubble is formed at the end of a capillary (1) produced by a special process. Its growth is limited by a rejection area (2). The capillary is preceded by a chamber (humidifier) in which a few drops of the sample solvent can be placed. The size of the chamber is chosen such that the air becomes saturated with the solvent vapour as it passes through the chamber.

### III Construction and start-up of the maximum pressure tensiometer MPT 2

#### III.1 Instrument description

The arrangement of the instrument is shown schematically in Fig. 3.1. Air is blown from a controlled pump (1) through a filter (2), a throttle capillary (3) and a larger chamber through the measurement capillary (4) into the test liquid (9). The volumetric air flow is measured with the differential pressure
sensor (5) across the capillary (3). The pressure at the inlet of capillary (4) is equal to the maximum internal bubble pressure and is measured with the pressure sensor (6). A microphone (7) is used to determine the time interval between the bubbles. The signals of these sensors are processed by a control unit (11) and passed on to a computer (12).

Fig. 3.1: Schematic arrangement of the maximum pressure tensiometer MPT 2

1.- Pump  2.- Filter  3.- Throttle capillary  4.- Measurement capillary  5.- Differential pressure sensor  6.- Pressure sensor  7.- Microphone  8.- Sample cell  9.- Sample  10.- Thermostating vessel  11.- Electronic control unit  12.- Computer

Fig. 3.2: Schematic arrangement of the maximum bubble pressure tensiometer MPT 2

1 - Mechanical unit of the maximum pressure tensiometer MPT 2  5 - Connecting cable MPT 2-M - MPT 2-E  6 - Connecting cable MPT 2-E - computer  7 - Computer  8 - Connecting cable MPT 2-M - electrical measuring head  9 - Electrical measuring head  10 - Capillary for electrical measuring head
Fig. 3.3: Mechanical unit of the MPT 2
1 - Housing
2 - Adjustable feet
3 - Measurement capillary
4 - Humidifier
5 - Sample cell
6 - Sample
7 - Thermostating vessel

Fig. 3.4: Electronic unit
1 - Main switch
2 - Indication for communication between electronics and computer
3 - Indication for taring
4 - Indication for tare menu
5 - Indication of operating status
6 - Indication for bubble detection
7 - Indication for electrical bubble detector
8 - Switch between electric and acoustic bubble detector
9 - Indication for acoustic bubble detector
10 - Reset button
In addition to the acoustic detection of the bubble interval it is also possible to detect the time between two bubbles by using a conductivity sensor. This requires a special measuring head, a connecting cable between measuring head and the tensiometer, and a special measurement capillary.

The maximum pressure tensiometer consists of a mechanical unit and the electronics which are linked together by a cable (Fig. 3.2). Fig. 3.3 is a schematic diagram of the mechanical unit and Fig. 3.4 that of the electronics.

Table 3.1 lists the components of the maximum pressure tensiometer MPT 2 together with their order numbers, as well as the standard accessories (included in the instrument price). Table 3.2 lists optional accessories for the maximum pressure tensiometer with their order numbers, while Table 3.3 gives the technical details of the maximum pressure tensiometer MPT 2. The computer is not part of the equipment as supplied; it can however by supplied if required. Any PC-Pentium is suitable as computer. However, computers of less capacity are not recommended as the new MPT 2 software is a WINDOWS application and requires a sufficient performance. It should be a Pentium or higher with Windows 95 or higher.

Table 3.1: Parts of the maximum pressure tensiometer MPT 2 (standard accessories)

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Standard accessory</th>
<th>Order No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>electronic unit (MPT 2-E)</td>
<td>LMT 831</td>
</tr>
<tr>
<td>1</td>
<td>mechanical unit (MPT 2-M)</td>
<td>LMT 932</td>
</tr>
<tr>
<td>2</td>
<td>Measurement capillary (standard)</td>
<td>LMTZ 915</td>
</tr>
<tr>
<td>1</td>
<td>Glass thermostating vessel</td>
<td>EG 047-1</td>
</tr>
<tr>
<td>1</td>
<td>Connecting cable MPT 2-E-MPT 2-M</td>
<td>UK 170</td>
</tr>
<tr>
<td>1</td>
<td>Main supply cable for Europe</td>
<td>EKN 006</td>
</tr>
<tr>
<td>1</td>
<td>Main supply cable for USA</td>
<td>EKN 010</td>
</tr>
<tr>
<td>1</td>
<td>RS232 connecting cable</td>
<td>EKS 037</td>
</tr>
<tr>
<td>1</td>
<td>Software MPT 2 (German)</td>
<td>LDTD 4011</td>
</tr>
<tr>
<td>1</td>
<td>Software MPT 2 (English)</td>
<td>LDTE 4011</td>
</tr>
<tr>
<td>1</td>
<td>Set beakers 50 ml</td>
<td>EG 004</td>
</tr>
</tbody>
</table>

Table 3.2: Other accessories for the maximum pressure tensiometer MPT 2

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Other accessory</th>
<th>Order No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Measuring head, electrical</td>
<td>LMTZ 910</td>
</tr>
<tr>
<td>1</td>
<td>Capillary (only together with LMTZ 910)</td>
<td>LMTZ 911</td>
</tr>
<tr>
<td>1</td>
<td>Capillary (hydrophobic)</td>
<td>LMTZ 919</td>
</tr>
<tr>
<td>1</td>
<td>Humidifier</td>
<td>EG 049</td>
</tr>
<tr>
<td>1</td>
<td>Glass thermostating vessel 60 cm high</td>
<td>EG 047-3</td>
</tr>
<tr>
<td>1</td>
<td>On-line flow cell</td>
<td>UD 403</td>
</tr>
<tr>
<td></td>
<td>LAUDA heating and cooling thermostat</td>
<td>on request</td>
</tr>
</tbody>
</table>
Table 3.3: Technical data of the maximum pressure tensiometer MPT 2

<table>
<thead>
<tr>
<th></th>
<th>Dimensions</th>
<th>Technical data MPT 2</th>
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<tbody>
<tr>
<td>Measuring range</td>
<td>mN/m</td>
<td>10 - 100</td>
</tr>
<tr>
<td>Reproducibility of surface tension</td>
<td>mN/m</td>
<td>0.1</td>
</tr>
<tr>
<td>Absolute accuracy of surface tension</td>
<td>%</td>
<td>0.25</td>
</tr>
<tr>
<td>Dynamic time range</td>
<td>s</td>
<td>0.0001 - 100</td>
</tr>
<tr>
<td>Reproducibility of time range: 0.1 sec – 100 s</td>
<td>%</td>
<td>5</td>
</tr>
<tr>
<td>0.01 sec - 0.1 s</td>
<td>%</td>
<td>10</td>
</tr>
<tr>
<td>0.001 sec - 0.01 s</td>
<td>%</td>
<td>20</td>
</tr>
<tr>
<td>0.0001 sec - 0.001 s</td>
<td>%</td>
<td>25</td>
</tr>
<tr>
<td>Temperature range</td>
<td>°C</td>
<td>0 ... 90</td>
</tr>
<tr>
<td>Sample quantity</td>
<td>ml</td>
<td>6/12</td>
</tr>
<tr>
<td>Dimensions (W x D x H): - electronics (MPT 2-E)</td>
<td>mm</td>
<td>340 x 270 x 105</td>
</tr>
<tr>
<td>- mechanical unit (MPT 2-M)</td>
<td>mm</td>
<td>220 x 240 x 240</td>
</tr>
<tr>
<td>Weight:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- electronics (MPT 2-E)</td>
<td>kg</td>
<td>4.2</td>
</tr>
<tr>
<td>- mechanical unit (MPT 2-M)</td>
<td>kg</td>
<td>8</td>
</tr>
<tr>
<td>Power consumption</td>
<td>W</td>
<td>75</td>
</tr>
</tbody>
</table>

**III.2 Connecting up the components of the maximum bubble pressure tensiometer MPT 2**

The components of the maximum pressure tensiometer MPT 2 (MPT 2-M and MPT 2-E) are connected together according to Fig. 3.2 using the cables supplied. The electronics MPT 2-E is linked to the serial interface of the computer using an additional cable. The electronics MPT 2-E is connected to the electrical supply.

**III.3 Installation of the Software for WINDOWS 95/98**

Before using the instrument the software coming with the instrument has to be installed. The software is a modern WINDOWS application and gives a number of useful tools to the user which allow a further elaboration of measuring results by designing graphs with various options and a report of the measured data in a format which can be controlled by the user in a wide range.
The installation is simple and has to be performed in the following sequence:

1. From the WINDOWS surface start the programme Install.exe either
   a) via the Explorer by double click on this icon
   b) via Start – Execute

2. In the opened window, the name of the programme folder (default C:\MPT) can be defined; by clicking with the mouse on either “New group” or “Existing group” the MPT programme is copied into the selected programme group (New group is recommended).

3. If “Existing group” is selected, all programme groups are listed up and the appropriate one has to be selected via mouse click.

4. After clicking “OK” the programme files and folders are copied and the software is ready for use. After rebooting the system, the new programme group is available.

The copied files comprise:
5. You may move the MPT icon directly onto the WINDOWS surface in order to start the programme easily. It is recommended to create subdirectories for the experimental data, such as it was arranged by the installation routine, which created the subdirectory “..\DATA”.

IV Description of the Software

IV.1 Start of the program

The program is started by either clicking on the icon on the Windows surface or via Start/Program/MPT. The screen of Fig. 4.2 appears.

IV.2 Start of a measurement

Before each start of a measurement the mode “Measurement” has to be selected (Fig. 4.1).

Fig. 4.1: Pull down menu for selection of Working mode

The measurement is started then via „Measurement“, „Open“ or “Start” (cf. Fig. 4.3) or via pressing the bottom shown in Fig. 4.2. The start leads to the standard window “Save as” of Fig. 4.4.

Fig. 4.2: Initial screen of the MPT 2 software
Fig. 4.3: Pull down menu "Measurement"

The file select box allows you to name the file into which the measurement data will be stored during the experimental run.

Fig. 4.4: File select box to place and name the data file of the measurement

If the chosen file name already exists the program gives a warning (Fig. 4.5).

Fig. 4.5: Warning if a file name is going to be chosen twice

After "OK" the input window of Fig. 4.6 is opened to insert the parameter values of the actual measurement.

IV.2.1 Parameters of the measurement

The dialog box “Parameter of experiment” of Fig. 4.6 opens when you start a new experiment. The strategy of the measurement can be designed here.

Fig. 4.6: Dialog box for inserting the details of the measurement
The following measurement parameter can be inserted:

**Number of actual capillary**
For a proper run of the measurement the program needs the parameter of the capillary and the parameter of measurement (see VII.5.3). Four different capillaries can be used for the measurement. Each of them has unique parameters. Both sets of parameters (capillary and measurement) ought to be determined beforehand.

**Measurement mode**
Defines the procedure in which the measurement is performed. Five different modes can be stored, which can be later selected by clicking on the button (for more details see VII.4.8). When inappropriate values are chosen in the design of the measurement mode, a window shows the available interval for the respective parameters. Previously assembled procedures can be selected from the drop down menu.

**Sample characterisation**
In this box you can input text to define the properties of the sample liquid.

**Density initial/meas**
In these two boxes you input the density values of the sample liquid at room and experimental temperature, respectively.

**Concentration**
This box contains additional information on the sample concentration of the studied substance.

**Temperature**
Defines the temperature at which the experiment is to be performed.

**Viscosity**
Put in the actual viscosity of sample. In case it is unknown the value 1.0 for water should be used.

**Surface tension of solvent**
This value is used when the capillary radius is determined via a calibration measurement with the solvent, for instrument test, and for the estimation of the critical point in the P(L) dependence.

**Additional info**
In this box one can input any additional information.

### IV.2.2 Measuring mode

By pressing the bottom in the window “Parameters of the experiment” the window for the measuring mode is opened.
This window allows to program the course of the experimental run. Five modes are preset and can be selected via the numbers “1” to “5”. More details on the optimum use are given in section VII.5.

**Start mode:** Selection of the way how to start the measurement: “Pumping” or “Preliminary pumping”. If one wants to avoid the measuring liquid to penetrate into the capillary, preliminary pumping must be selected.

If the Pumping mode is selected, after the start the compressor produces an extra air pressure to push out the liquid risen into the capillary. At Preliminary pumping the program allows to connect the capillary to the device and the compressor produces an extra air pressure. After it has reached a sufficiently high value the program asks to immerse the capillary into the liquid. The extra air pressure prevents the liquid from penetrating into the capillary.

**Mode of flowrate change:**

This function allows to select the way of changing the flowrate (or any combination of different modes):

- **Decrement**
  - Flowrate goes down
- **Increment**
  - Flowrate goes up
- **Linear**
  - Flowrate will change in a monotonous and continuous way
- **Step**
  - Stepwise change of the flowrate from point to point
- **Stop**
  - The regime of stopped flowrate. After the sudden termination of the air supply at first bubbles are formed due to extra pressure and thereafter due to the decrease in surface tension which is connected with an increase in the bubble formation time
- **Constant**
  - Flowrate remains unchanged over the whole measuring procedure
Relative change of air flowrate: To get an equal number of points over the whole measuring interval the steps of flowrate changes have to be different at each flowrate. It is equal to the given value only at a flowrate of 100 mm³/s. If the value is given in %/step the flowrate value at each subsequent point will differ from the value in the previous measured point by the given amount. For a value given in %/min each subsequent flowrate will be increased (or decreased, according to the direction of flowrate change) approximately by the given percentage.

Period of point setting: Defines the time interval between two subsequent points

Limit time for stopped flowrate: Defines the longest time of a single measurement in the stopped flow regime

Bounds of flowrate change: Defines the limits in which the flowrate can be changed

Once the parameter are selected they are valid also in subsequent measurements unless their values are changed again.

By confirming the selections made in the windows “Measuring mode” and “Parameters of the experiment” by “OK” the measurement starts, except the pass through “Measurement/Start” (Fig. 4.3) was not used. In these cases a start via the main menu is required (Fig. 4.2).

IV.3 Process of measurement

Prior to the first start of a measurement the program performs a zero taring procedure every day (Fig. 4.10). Thus it is recommended to perform the first measurement with water. All subsequent measurements at this day start immediately.

![Image](image-url)
IV.3.1 Presentation of the measuring results

During the measurement (Fig. 4.13) the actual values of the measured time $T$, pressure $P$ and flowrate $L$ are shown in the respective boxes of the main screen. Also in the graph and the table the measured values are shown in real time. Both windows can be opened via the menu “View” (Fig. 4.11) or preselected (cf. Fig. 4.12). The same menu allows the activation of the screensaver manager working under the actual WINDOWS parameters. If the screensaver is passive it doesn’t switch on/off while the program works.

![Menu to select the opened windows](image)

![Selection of the measurement graph and the respective table](image)

During all operating states (the current process: measuring, testing, taring, etc.) it is possible to exit the actual mode via the interrupt button [Stop]. The measurement can later be continued at the
same point or at any other point. The point for continuation is selected by input of the corresponding set-point for the flowrate (via pull down menu “options” in the main menu (cf. IV.5.2)).

IV.3.2 End of a measurement

When a measurement is finished the information message of Fig. 4.14 appears. Confirmation “OK” opens the window of Fig. 4.15. When you got enough points in jet and bubble range you press the button “repeat”. Now the program put the lines into the graph (Fig. 4.16). After finishing a measurement the results automatically are saved into the earlier selected file.

Fig. 4.14: Measurement terminated

Fig. 4.15: Selection window for the detection of the critical point

Fig. 4.16: Dependence P(L) with the determination of the critical point (intersection of the two red lines)

IV.3.3 Bottoms in the main menu

The main menu contains the following functional bottoms for a quick and easy handling without using the pull down menu:
Maximum Bubble Pressure Tensiometer MPT 2

IV.4 Data Interpretation

To interpret the results of a measurement one has to switch via the main menu from “Measurement” to “Graph” (cf. Fig. 4.1 and 4.2) which leads to the screen of Fig. 4.17. In this window a large variety of graphic tools are available. The physical background of the different functions is explained in section VII about the scientific meaning of the dynamic surface tension and its interpretation.

IV.4.1 Graphic interpretation

Fig. 4.17: Screen showing both the graphic window and the table with the measurement results in the mode “graph”
Fig. 4.18: Menu “Measurement/Open”

Fig. 4.19: Window for the graphic design of the printout

Fig. 4.20: Data point handling item “Edit”

Fig. 4.21: Pull-down menu “View”
Fig. 4.22: Selection of the function

Fig. 4.23: Selection of the polynom

A graph given as example in Fig. 4.17, can be designed by using the accessible tool. Via pull down menu “file” a file which is opened can be designed and printed. To arrange the printout the scaling, the colour and the orientation of the graph can be selected.

Via the menu “Edit” (Fig. 4.20) the graph can be further handled. Points falling out of the row due to disturbances during the measurement can be erased by the function “Delete Point”. If “Show Deleted Points” is selected all deleted points are shown. With “Restore All Points” all deleted points can be returned to the set of data. Fig. 4.22 allows to select the proper function for the measurement presentation. The points can then be approximated by a polynom of a certain degree (from a linear regression to a polynom of 8 degree).

The functions available via the menu are the following:

- **Open**: loads existing experiment file.
- **Close**: closes one of the loaded experiments.
- **Print**: prints the graph of the actually processed experiment.
- **Scale of print**: adjusts the dimensions of hard copy in respect to the dimensions of the sheet.
- **Exit**: exits the MPT experiment viewer.
- **Delete Point**: deletes a point marked previously with the mouse.
- **Show Deleted Points**: shows all previously deleted points.
- **Restore all Points**: restores all previously deleted points.
<table>
<thead>
<tr>
<th>Function</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Create Report</td>
<td>creates the report using the data of the actually processed experiment.</td>
</tr>
<tr>
<td>Function</td>
<td>selects one of the available plots.</td>
</tr>
<tr>
<td>P/L</td>
<td>shows the graph in pressure-flowrate coordinates.</td>
</tr>
<tr>
<td>T</td>
<td>shows the graph in $\sigma$–$t$ coordinates.</td>
</tr>
<tr>
<td>1/T</td>
<td>shows the graph in $\sigma$–$t^{-1}$ coordinates.</td>
</tr>
<tr>
<td>ln(T)</td>
<td>shows the graph in $\sigma$–ln $t$ coordinates.</td>
</tr>
<tr>
<td>$T^{1/2}$</td>
<td>shows the graph in $\sigma$–$t^{1/2}$ coordinates.</td>
</tr>
<tr>
<td>$T^{-1/2}$</td>
<td>shows graph in $\sigma$–$t^{-1/2}$ coordinates.</td>
</tr>
<tr>
<td>ST/Time</td>
<td>shows the graph in $\sigma$–$T$ coordinates, where $T$ is the time elapsed from the start of the experiment up to the moment of bubble formation.</td>
</tr>
<tr>
<td>P/Time</td>
<td>shows the graph in the $P$-$T$ coordinates, where $T$ is the time elapsed from the start of the experiment up to the moment of bubble formation.</td>
</tr>
<tr>
<td>Time</td>
<td>selects one of the available times scales:</td>
</tr>
<tr>
<td>Life</td>
<td>uses the actually measured time for the graph.</td>
</tr>
<tr>
<td>Effective</td>
<td>uses the effective, specially calculated, time for the graph.</td>
</tr>
<tr>
<td>Manual scaling</td>
<td>scales according to a particular range to be shown in the graph.</td>
</tr>
<tr>
<td>Unzoom</td>
<td>cancels the action of the Zoom commands.</td>
</tr>
<tr>
<td>Zoom</td>
<td>assigns the left mouse button for a Zoom function. Press the left button in any point of the graph, holding it down and moving the mouse selects the desired region of graph to be shown. The respective graph will be drawn after leaving the left mouse button.</td>
</tr>
<tr>
<td>Select Point</td>
<td>gives the left mouse button the feature to mark a point.</td>
</tr>
<tr>
<td></td>
<td>To mark a point do the following:</td>
</tr>
<tr>
<td></td>
<td>Press the left mouse button at any place of the graph and the nearest point will be marked by a small circle.</td>
</tr>
<tr>
<td>Select critical P</td>
<td>gives the left mouse button the feature to assign the critical pressure.</td>
</tr>
<tr>
<td></td>
<td>To assign the critical pressure do the following:</td>
</tr>
<tr>
<td></td>
<td>Press the left button at any place of the graph; holding it down and moving the mouse selects the desired position of the horizontal line. After leaving the left button the graph will be redrawn taking into account the new value of the critical pressure. This function works only in the P-L mode.</td>
</tr>
</tbody>
</table>
View value gives the left mouse button the feature to calculate the value of the function and its derivation for the selected point. This feature is available only after an approximation has been performed.

To use this operation make the following:

Press the left button in any area of the graph, holding it down and moving the mouse to select the desired vertical line. The report window has to be opened before in order to transfer the points to the report file. If in the report options (see Fig. 4.17) the ‘Add calc point’ check button is ON then after leaving the button the dialog window ‘Add calc point to report?’ appears. The approximation function, calculated values of this function and its derivative to the selected point will be displayed in this window. If you select OK, the values of the marked point will be appended to the report. This function does not work in the P/L mode.

Select approx. Region gives the left mouse button the feature to select the region in which the approximation curve will be calculated.

To use this operation make the following:

Press the left button in any area of the graph (this position will be the beginning of the approximation region), holding it down and moving the mouse selects the desired approximation region. After leaving the left button the approximation curve will appear in the graph. This feature does not work when the graphic mode P/L is selected.

The same functions can be reached via functional bottoms:

- loads an existing experiment
- closes one of the loaded experiments
- creates a report from data of the actually processed experiment
- selects the region for the polynomial approximation
- views the value of a point indicated by the mouse
- shows graph in pressure-flowrate coordinates
- shows graph in $\sigma$–t coordinates
- shows graph in $\sigma$–t$^{-1}$ coordinates
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- shows graph in $\sigma$–ln(t) coordinates
- shows graph in $\sigma$–t$^{1/2}$ coordinates
- shows graph in $\sigma$–t$^{-1/2}$ coordinates
- shows graph in $\sigma$–T or P-T coordinates, where T is the time elapsed from the start of experiment up to the moment of bubble formation. The format of the graph depends on the ticked item in the menu View/Function.
- switches time representation: effective or real bubble formation time.
- assigns the left mouse button for a Zoom function. Press the left button in any point of the graph, holding it down and moving the mouse selects the desired region of graph to be shown. The respective graph will be drawn after leaving the left mouse button.
- cancels the actions of Zoom commands.

IV.4.2 Preparation of a report

To make a report the item “Create Report” has to be selected (cf. Fig. 4.20) and the window of Fig. 4.24 appears.

Fig. 4.24: Window to select all items of the measurement report

After marking the appropriate boxes and pressing OK the report of the actual experiment appears.
By selecting the respective function in the menu “Report” (cf. Fig. 4.26) the results of the experiment can be saved under a given name, copied into the clipboard etc. The file name proposed by the program is the one selected for the experiment, but having the extension “txt”.

**IV.5  Settings, check and calibration of the device**

**IV.5.1  Inspection and change of capillary data**

The capillary data can be shown via the menu “options” (Fig. 4.27) in the main screen of Fig. 4.2 in case the program is in the measurement mode. The window “Parameter of capillary” will be opened (Fig. 4.28). If a file is open, the capillary data can only be read, while in case when no file is open the data can be overwritten. The last step should be made only by experienced users or in accordance with the supplier.
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IV.5.2 Options of the measurement

If one selects the menu item “Options/Parameter of meas.” (measurement interrupted, file not closed yet, cf. Fig. 4.7) then the limits of the measurement can be set for which additional points will be measured. Other conditions of the experiment can also be varied here. Moreover again the capillary data can be shown here and the COM port selected (4.29).

IV.5.3 Calibration of the device

The test of the correct functioning of the device, auto-calibration and estimate of the measurement precision can be done in two different modes and with respect to different device functions. The test can be started via the menu “Measurement”.

Fig. 4.28: Window for setting the capillary parameters

Fig. 4.29: Selection of the RS232 port to which the instrument is connected

Fig. 4.30: Selection of the calibration

Fig. 4.31: Selection of the test type
**Express test:**

Here the calibration of pressure sensors, the check of the capillary's cleanliness (via stability of bubble formation) and the surface tension measurement at a bubble formation time of about 0.5 s are performed during the test. The steps are as follows:

1st step:

![Choose correct capillary](image1)

**Fig. 4.32:** Choose correct capillary

2nd step:

![Fill the cell with water](image2)

**Fig. 4.33:** Fill the cell with water

3rd step (after OK the measurement starts)

4th step:

![Test value for the surface tension](image3)

**Fig. 4.34:** Test value for the surface tension of the water sample is given

After OK the program returns to the main menu.

**Full test**

![Full test](image4)

**Fig. 4.35:** Full test

The complete testing procedure comprises more functions than the express mode: taring of the device, performance of a measurement and calculation of the correction coefficients, the deadtime, the bubble volume and the equilibrium pressure.
1st step:
If the capillary is not adjusted before, a warning window is given to inform about it.

Fig. 4.36:  Informing window

2nd step:
After input of the name and parameters of the measurement a appears and asks to fill in the test solvent, generally water.

Fig. 4.37:  Hint to fill the cell with distilled water

3rd step: After filling and “OK” the measurement is performed.

4th step: After completion the window of Fig. 4.14 appears.

5th step: The window for determining the critical point appears (Fig. 4.15). When selecting “Repeat” the critical point is determined (Fig. 4.38). The critical point is found when at least 4 points have been measured in the jet regime and a bubble interval of about 1 second has been reached. The critical point is essential for the determination of the deadtime $t_d$ (cf. section VII.4.5).

Fig. 4.38:  Result of a successful device test
6th step: The new values should be close to the once determined earlier. If this is not the case, the data of calibration can be stored and are used in subsequent measurements. The table contains all new determined values of the correction coefficient, the equilibrium pressure, the initial flowrate, the bubble volume and the deadtime.

IV.5.4 Capillary testing

If this menu item is selected, the check of the capillary’s cleanliness (via stability of bubble formation) at a constant flowrate is carried out before each measurement.

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**Fig. 4.39:** Cleanliness test of the capillary required for accurate measurements

The bubble time at this test is of the order of 1 second. When the bubble volume deviates from the stored value, the actual value will be given in the table of actual experiment and this actual value used for the calculation of the present measurement. As long as the capillary is not subjected to impurities from the sample, the capillary test should be active any time.

When the bubble production is unstable you get a warning (Fig. 4.40).

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**Fig. 4.40:** Information on an non-regular bubble formation

IV.6 Device test

The device test can be activated via the main menu (Fig. 4.1 and 4.2). Then the test is called (Fig. 4.41).

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**Fig. 4.41:** Menu “Device test”
IV.6.1 Check of tightness

The air-tightness of the measuring system, given by a number of sealings, has to be checked in particular for the stopped flow regime.

IV.6.2 Calibration

Sensor of flowrate and pressure will be calibrated.

IV.6.3 Valve switch

The device valves can be switched into one of 3 regimes: work, calibration, air-tightness check:

- Measurement
- Calibration
- Check in air

IV.6.4 Flowrate setting, Measurement of P, L, and Measurement of T

If the “Flowrate” item is chosen, the desirable flowrate can be set up in the edit line “Pumping” and this value can be transferred to the device by clicking on the “Start” button. The item “P, L” activates pressure and flowrate measurements. The measurements are carried out continuously and are shown approximately each second. To exit from the regime click on “Stop”. The measurements of the bubbles formation period can be carried out continuously when selecting “T”. The results are shown in accordance with the bubble registration. If the measured value is less than 0.05s or exceeds 1s it will not be shown. To terminate these functions click on “Stop”.

IV.7 Help

Via “Help” information on the MPT 2 can be obtained.

Information

The Copyright and the program version of the MPT software are shown.

Users Help

Calls the help system.

V Possible errors in the operation of the tensiometer MPT 2

V.1 Connection between MPT 2 and PC

If the MPT 2 software is started while the instrument is not switched on a message appears. The user has to check if the device is switched on and the connection to the PC is Ok.

Fig. 5.1: Error message: no connection to the instrument
A similar message appears when the connection between device and PC is interrupted.

**V.2 Instrument warning by control lamp**

Irregular bubble formation can be recognised by an irregular flashing of the indicator lamp 6 (cf. Fig. 3.4). A group of bubbles is followed by a longer pause.

The reason for uneven bubble formation is contamination of the capillary. This may be caused, for example, by storing the capillary in plastic bags (plasticiser migrates to the surface of the capillary) or by touching the front face of the capillary with a finger. The capillary must be cleaned thoroughly.

For thorough cleaning the capillary is placed for approx. 5 min into a cleaning liquid in an ultrasonic cleaning bath. A suitable cleaning fluid is e.g. chrome-sulfuric acid or a similar strongly reactive liquid. It is essential however that the cleaning fluid is not alkaline.

After cleaning in chrome-sulfuric acid (or a similar liquid) the capillary is rinsed several times in water in an ultrasonic bath. After a series of measurements the capillary has to be cleaned in the ultrasonic bath using the solvent of the sample. Between measurements the capillary is stored in distilled water or in the solvent most frequently used for the measurements.

With some samples it is necessary to dry the capillary before the measurement using a volatile solvent. It is important here to use a pure solvent. Any solvent traces remaining on the capillary can affect subsequent measurements.

**V.3 No straight line in the graph P(L)**

If the program does not produce a straight line in the graph P(L) (cf. for example Fig. 4.17), an insufficient number of points has been measured above the equilibrium pressure. At least 4 points above this equilibrium pressure are required which have to lay on a straight line. In order to bypass this problem subsequent measurements should be started at a flowrate higher than that used in the failed measurement.

If a solvent other than water is used, the surface tension of this solvent has to be entered via the window “Parameter of experiment” (Fig. 4.6). The equilibrium pressure of the solvent used is calculated for this surface tension.

**V.4 Jumps in the measured surface tensions**

If the measured surface tensions exhibit jumps, this indicates contamination of the capillary. The capillary has to be cleaned with the sample solvent in an ultrasonic cleaning bath, and the respective range has to be investigated again.

If the jumps appear reproducibly this indicates the formation of monolayers on the capillary. The capillary should then be cleaned again carefully in the sample solvent or another cleaning solution. Reactive liquids such as chrome-sulfuric acid should not be used too often as they tend to induce activation of the capillary glass surface.
V.5  Further error messages

An information message appears when the instrument runs and due to any reason the connection between PC and MPT 2 is interrupted.

Fig. 5.2: Connection between PC and MPT 2 does not work

If the gas system is not tight, a message informs about it. The most probable leakage is the stopper of the measuring cell. Put few drops of the solution to seal.

Fig. 5.3: Message when problems with gas leakage exist

Further error massages can appear during the use of the instrument.

Fig. 5.4: Problems with the capillary

Please check the capillary and clean according to the recommendations given above.

Fig. 5.5: Problems when writing to the harddisk or diskette

Check if there is enough free space on the harddisk or diskette.

VI  Tips and tricks for user of the MPT 2

This section is for all those users who want to optimise the handling of the maximum bubble pressure tensiometer MPT 2. These tips and tricks have been supplied from users with long time experience in the daily use of the MPT 2 and its predecessor MPT1. It will be particularly helpful for all those users who are going to study systems which do not belong to the so-called standard solutions. There are systems, where the optimum experimental conditions can only be found by trial and error rather than by a “recipe” valid for any liquid. The given hints intend to be a support in this procedure.
VI.1 Control of the appropriate recording of the capillary parameters

The immersion depth of the capillary into the solution is chosen and controlled by the user. Using the standard beakers 10 ml (see mark) correspond to an immersion depth of 2.5 mm. The immersion depth can also be measured by a cathetometer or ruler using the mark placed at the capillary. It should be kept in mind that the measurement of the immersion depth needs not to be very precise: it is quite sufficient to measure this value to about ± 0.25 mm. Any small error will subsequently be compensated during the calibration process using the liquid of known surface tension (procedure: Device testing - Full). The important requirement here is that in all experiments that follow the testing, the same liquid volume is used. For viscous or foaming solutions it is recommended to increase the capillary immersion depth to 5-8 mm. Surely, and the calibration should be performed for these conditions then. The increased immersion depth expedites the separation of bubbles in viscous solutions, or prevents a complete foaming of the liquid.

The equilibrium pressure is the pressure which corresponds to the surface tension of water at room temperature. For a capillary of radius $r_{\text{cap}} = 0.075$ mm and the standard immersion depth, the equilibrium pressure is around 1950 Pa.

The initial flowrate for the time measurements is calculated by the program from the bubble volume as $V_b/0.08$ s. In this flowrate range, precise measurements of the time interval between two bubbles by the acoustic or conductometric sensor is ensured. However, the user can adjust (either increase or decrease) this value. If the initial flowrate (expressed in mm³/s) exceeds 15 times the bubble volume (expressed in mm³), then the program regards the results of the measurement as unreliable. In this case, an internal procedure is used which calculates the time intervals from the actual flowrate and the average volume of the bubbles in the current experiment.

The accuracy of the recording of the capillary resistance coefficient can be verified as follows. Insert a dry capillary into the dry cell (the stopper should be wetted with 2 to 3 drops of water), adjust the flowrate to 100 mm³/s (procedure: Device test - Flowrate setting), and perform the pressure measurements (procedure: Device test - Measurement P, L). The result obtained (say, 1500 Pa), divided by the flowrate value (100 mm³/s), yields the capillary resistance coefficient (15 for this case). This parameter is used in the procedure which verifies the correct determination of the location of the critical point in the dependence P(L) (to compare the experimental value of the slope in the jet regime with the theoretical value).

The cell factor is employed by the program for the corrections of the hydrostatic pressure, when the measurements are performed at temperatures above or below room temperature. This “Factor of cell” is calculated as the ratio of the volume of liquid contained in the cell (expressed in mm³) to the cross-
section area (expressed in mm$^2$) in the place where the capillary tip is located. For a cylindrical cell this factor is equal to the liquid height in the measuring cell.

The deadtime value is calculated by the program from the flowrate value at the critical point in the plot of pressure versus flowrate $P(L)$ and the bubble volume $V_b$ as $V_b/L_c$. For standard capillaries and usual bubble volumes the deadtime amounts to about 30 ms. This time is employed in the calculations of surface lifetime for the experiments where the critical point remains unmeasured (all points correspond to the bubble regime.)

**VI.2 Functional testing of the device.**

The Device testing (Express or Full) procedure is used to check the functioning of the device. Fill the cell with purified water or another solvent to be used to prepare the solutions. It is recommended beforehand to ensure that no air leakage takes place (regime: Device test - Check of tightness). To eliminate possible air leakage, the stopper between the cell and the device should be wetted by 2 to 3 drops of water (solvent). In the Express regime only the surface tension is checked. We recommend this operation to be performed daily, just after the device is switched on. If the result is close to that recorded previously during the Full procedure, this new value of the calibration coefficient needs not be stored. In the Full regime, the bubble volume and deadtime values are also determined. As the deadtime is calculated from the critical point in the pressure versus flowrate plot, the maximum flowrate in these experiments should exceed the critical value $L_c$ by 30-40 mm$^3$/s. The Full operation should be performed each time a new solvent is used, or the capillary immersion depth is changed, but in any case at least once a week in order to ensure full functioning of the instrument.

**VI.3 Optimisation of the experiment parameters**

For running an experiment various settings are required which are performed in the modes Measurement-Start-File-Parameter of the Experiment-Measurement mode, and the Options-Experiment- Parameter of Measurement.

**VI.3.1 Parameters of the experiment**

In the table of experimental parameters there are some values which affect the results of measurements significantly. Therefore it is necessary to verify that correct values are recorded. There are two relevant values of the density of liquid: the initial density (at room temperature) and the density at experimental conditions (at the temperature of the thermostat). If measurements are performed for the same liquid sample at different temperatures, then from the two density values the correct value of the hydrostatic pressure is automatically calculated. For example, the measuring cell is filled with hexane (the capillary immersion depth is, say, 4 mm) at the temperature 20°C and density 0.66 g/cm$^3$,
but the measurements are performed at 60°C, where the density of hexane is 0.62 g/cm³. Using the Factor of cell (see Parameter of capillary) the program stores the correct value of the hydrostatic pressure.

The viscosity of the studied liquid is used to introduce corrections to the values of surface tension and bubble lifetime caused by the liquid viscosity in the time range below 0.01 s. If measurements are performed with aqueous solutions at room temperature, then a value of 1 should be used.

Surface tension of the solvent (water) is used to make a rough estimate of the critical point in the pressure versus air flowrate co-ordinates P(L).

If the measurements are to be performed with liquids which should not penetrate into the capillary (colloidal solutions and suspensions, in particular protein solutions, enamels, paints etc.), the “Preliminary pumping” regime should be used as the “Start” mode. In contrast to the “Pumping” regime, in the preliminary pumping regime the capillary is introduced into the liquid only when an excess pressure in the system is already created. The user should watch the information on the computer screen, so that the immersion of the capillary into the solution is made only when the corresponding message is displayed by the computer.

VI.3.2 Mode of flowrate change

Several regimes of the air flowrate into the capillary (Mode of flowrate change) are implemented in the program: with flowrate increase, with flowrate decrease, with constant flowrate, stopped flowrate regime, combinations of increasing or decreasing flowrate with the stopped flowrate regime. In addition, in the flowrate increase or decrease regimes, either stepwise (step) or continuous (linear) flowrate variation can be chosen.

What are the rules guiding the user to choose the correct flowrate variation regime? If a control of processes is performed happening in the long time interval (various technologic processes involving variations in surfactant concentration, hydrolysis kinetics of ionic surfactants, kinetics of various chemical reactions with the formation or destruction of surfactants, kinetics of dissolution of solid surfactants etc.), then the “Const” regime with a predefined air flowrate (predefined time interval between two bubbles) will be optimum. The user has to determine beforehand which interval will be the most informative. It should be kept in mind that the maximum number of measured points is 500, and the time interval between measured points can be chosen in the range between 10 to 1000 s (this refers to about 1 hour to roughly one week time).

For measurements in the long time range (1 to 100 s), the stopped flowrate regime “Stop” should be used. The total duration of this procedure can be chosen in the range of 1 to 30 min. We recommend to perform the recording up to 15 min. The maximum time interval (30 min) can be chosen for strongly surface active non-ionic surfactants, say oxyethylated alcohols or phenols. The measurement
procedure in this regime is stopped if the waiting time for one bubble exceeds 100 s. The recommended flowrate value (in this case the initial value) is 4 to 10 mm$^3$/s, with the lower value corresponding to surfactant solutions of low concentration, while higher values should be used for concentrated solutions.

For studies in the surface lifetime range < 1 s, increasing or decreasing flowrate regimes should be used. If mixtures of surfactants are studied, e.g. various technical compositions, then the increasing flowrate regime is recommended. In this case during the measurements in the long time range less foaming of the solution takes place, that is, the most surface active components of the mixture remain in the solution and are not transferred into the foam. At the same time, foaming in the short time range (large flowrate values) has almost no effect on the surface tension in this time range. For such solutions the combined regime with the stopped flowrate should be used: Stop + Increment step. On the contrary, when pure surfactants are studied, then the preliminary foaming of the solution decreases the extent to which the solution is polluted by highly surface active contaminations (e.g., higher homologues, or acids or alcohols formed due to hydrolysis of ionic surfactants). Therefore in these cases regimes with decreasing flowrates should be preferred. Recommended is again a combination with the stopped flowrate regime: Increment step + Stop.

In the stepwise regimes (step) the relative variation of the flowrate can be varied from 0 to 30% between the measurements. The higher the step, the smaller is the number of experimental points, and the longer is the period between the experimental points. This period depends on the step value: the larger the step, the shorter is the allowed time interval. The optimal step is between 3 and 10%. For concentrated solutions we recommend to use the minimum period of the flowrate establishment (10 to 20 s), while for low concentrated solutions (especially for highly surface active surfactants) this time should be 20 to 40 s.

In the regimes with continuous flowrate variation (linear), this flowrate varies between 0 and 50% per minute, while the interval between the experimental points does not depend on the flowrate variation, and can be chosen in the interval 5 to 30 s. These regimes can be used when results are promptly needed. We recommend to use maximum flowrate variations for strong concentrated solutions only, while for weakly concentrated solutions of highly surface active molecules this value should not exceed 30% per minute.

**VI.4 The measurement process**

The Capillary testing operation is useful for monitoring the device performance and the capillary quality. If in the Measurement menu this operation is marked, then it is performed at the beginning of each experiment. The program sets the interval between two bubbles of about 400 ms, using the bubble volume stored in the table of capillary parameters, and then determines the mean interval, maximum and minimum deviations, the mean bubble volume, and compares this value with the stored value. The entire operation requires not more than 1 min. The program also displays a warning
leakage in the device is observed (therefore do not forget about the wetting of the stopper before each experiment), or if the air flow through the capillary is blocked. From the values of deviations between the intervals, the user can conclude about the stability of the bubble formation process. Both the newly calculated value of the bubble volume, and that stored in the table Parameter of capillary, are displayed in the table of the current experiment. The newly determined value is used in the current experiment only, to control the measurement process. It should be noted that if the critical point position can to be determined in the experiment, then the bubble volume is not used to determine the lifetime or surface tension values. However, if all the experimental points are located in the bubble regime range, then for large flowrates the lifetime is calculated from the measured bubble volume.

The relative standard deviation of intervals, which is displayed in the table of the current experiment, is an important information on the stability of bubble formation. For aqueous surfactant solutions this parameter should not exceed 10%, while for non-aqueous solutions this parameter should not exceed 30%. If the standard deviation is higher, then the user should clean the capillary, as indicated in the manual. The relative standard deviation of the pressure for high quality capillaries and a correct choice of the measurement regime should not exceed 0.5%. If this parameter is higher (say 1%), and the standard deviation of the intervals is normal (10% or less), this can indicate that an inappropriate regime of flowrate variation is used. In this case one should either decrease the step of the flowrate variation, or increase the flowrate setting period. Note that in the Stop regime the standard deviations are not displayed, because the results are calculated from single bubbles. For regimes with increasing flowrate, the monotonous increase of pressure and monotonous decrease of intervals can also be regarded as a reliable indication of a correct experiment: for decreasing flowrate regimes for example this is true when a monotonous decrease of the pressure and a monotonous increase of the intervals is obtained. Another criterion of the reliability of the experiment is the approximately constant values of the interval by flowrate product for all measured points.