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Bubble Pressure Analyser BPA-1P



The bubble pressure tensiometer BPA-1P is a new development by SINTERFACE based on more than 10 years of experience in bubble pressure techniques, for example the MPT1 and MPT2 sold by LAUDA. Many new instrumental details have been published recently, such as the determination of bubble time characteristics, the optimisation of the aerodynamic system, as well as the options to reach extremely short as well as sufficiently long measuring times.

Main Principle of Bubble Pressure Tensiometry

The maximum bubble pressure method (MBPM) was proposed in 1851 (*M. Simon, Recherches Sur La Capillarité, Ann. Chim. Phys., 32(1851)5*) for measuring the surface tension of liquids. Later quite a number of instruments were set up, however, the handling was difficult and the accuracy low, until modern accurate pressure sensors have been developed. During the last 30 years the method was extensively improved and hundreds of scientific articles and reviews were published. Several companies in Europe and USA produce commercial devices of this type which are widely used in the scientific studies, in a wide range of industries (from metallurgy to food), in agriculture, pharmacology, medicine and ecology. A comprehensive description of the history and the present state of the art was described in a book chapter recently (*V.B. Fainerman and R. Miller, The maximum bubble pressure technique, monograph in "Drops and Bubbles in Interfacial Science", in "Studies of Interface Science", D. Möbius and R. Miller (Eds.), Vol. 6, Elsevier, Amsterdam, 1998, p. 279-326*).

The method is based on the measurement of the maximum pressure in a bubble growing at the tip of a capillary immersed into the liquid under study. When a bubble grows at the tip of a capillary, its radius of curvature decreases up to a hemisphere, and then increases again. Thus, at the hemispherical size the pressure measured is

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maximum. After the bubble passes this maximum pressure it grows quickly, separates from the capillary and a new bubble is formed.



The surface tension is calculated via the Laplace equation taking the capillary radius as radius of curvature:

$$P_{max} = 2 \gamma/r \tag{1}$$

When the capillary is immersed into the liquid with a depth h, the respective hydrostatic pressure is measured in addition:

$$P_{max} = 2 \gamma / r + \Delta \rho g h$$
⁽²⁾

 $\Delta \rho$ is the density difference of the liquid to air, and g is the gravity constant.

The time from the start of bubble growth to the maximum pressure at a hemispherical size is called lifetime t_i , and the interval from this hemisphere until bubble departure is called deadtime t_d . Both times together give the bubble time $t_b = t_i + t_d$. As the bubble surface grows during the experiment, the expansion has to be considered in the evaluation of the so-called effective surface age (see also the above mentioned monograph on bubble pressure tensiometry).

A schematic of the bubble pressure instrument BPA-1P is shown below. The pump produces a continuous gas flow, which is measured by the gas flow sensor. The gas flow capillary together with the gas volume damps the system and allows a smooth and regular bubble formation. The pressure sensor measures the pressure in the gas volume, which is proportional to the maximum pressure at the capillary tip. The pump and the two sensors are controlled by a computer via an electronic interface board.

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The PC also collects the measured data, calculates the dynamic surface tension and effective time and presents all results online. Only data in terms of the effective time can be used for compare and for complementation with data from other instruments.



Standard and Fast modus

The BPA-1P allows measurements in a standard and fast measuring modus. While the standard mode requires between 20 and 35 min, depending on the number of measured points, the fast modus measures a complete curve within 4-6 min. The results obtained by the two procedures are in perfect agreement as shown in the next figure for three Triton X-100 concentrations.



Dynamic surface tension for three Triton X-100 solutions, open symbols – Fast modus, closed symbols – Standard mode (several runs each)

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Corrections of the gravity effect

The surface tension γ is calculated from the modified Laplace equation

$$\gamma = \frac{r_{\rm cap} P_{\rm c}}{2} f , \qquad (3)$$

where $P_c=k(P-(gh)$ is the capillary pressure, k is an instrument constant, and the correction coefficient f is given by the polynomial

$$f = \sum a_i \left(\frac{r}{a}\right)^i$$
(4)

with the capillary constant

$$a = \sqrt{\frac{2\gamma}{\Delta\rho g}}$$
(5)

The coefficients of the polynomial read: $a_0 = 0.99951$, $a_1 = 0.01359$, $a_2 = -0.69498$, $a_3 = -0.11133$, $a_4 = 0.56447$, $a_5 = -0.20156$. If we define $x=r_{cap}/a$ we get from (5):

$$\frac{2\gamma}{\Delta\rho g} = \frac{r_{cap}^{2}}{x^{2}} \text{ or } \gamma = \frac{\Delta\rho g r_{cap}^{2}}{2x^{2}}$$
(6)

Together with (6) a relationship is obtained which let us directly account for the deviation of the bubble shape from sphericity:

$$\frac{\Delta\rho gr_{cap}}{P_c} = x^2 f(x)$$
(7)

The function f(x) yields the values shown in the figure below. We see that f changes by 6% in the given range of x. Neglecting this factor would lead to an error much larger than the experimental error of any instrument. The larger the capillary radius, the larger is this effect.



Course of the correction function f(x)

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Corrections of viscous effects

The correction implemented in the bubble pressure tensiometer BPA-1P goes back to studies made by *Fainerman, Makievski and Miller* (*Colloids Surfaces A,* 75(1993)229). These studies were performed with water/glycerol mixtures using a capillary of diameter 2 r_{cap} = 0.15 mm. The correction includes the calculation of the deadtime t_d (hence of the bubble lifetime t_l) and of the surface tension γ .

Corrected calculation of the deadtime t_d

The deadtime is increased when the geometry for bubble formation is kept constant and the liquid's viscosity increased. If the viscosity $\eta > 1 \text{ mm}^2/\text{s}$ (the value of water at room temperature), the bubble lifetime results to

$$t_1 = t_b - t_d (1 + 0.25 \ln \eta)$$

(8)

If, for example, η = 10 mm²/s, the deadtime is increased by a factor of 1.6 as compared to water. When the automatic correction is not wanted a value η < 0.5 mm²/s should be inserted as parameter value.

Corrected calculation of the surface tension γ

The surface tension correction depends on both the viscosity η and the bubble lifetime t_I. The correction works automatically in the BPA software when the viscosity $\eta > 0.5 \text{ mm}^2/\text{s}$. The corrected surface tension has to be calculated via the Laplace equation, where Δ is the correction value:

$$\gamma^* = \frac{r_c k(P - \rho g h)}{2} - \Delta \tag{9}$$

The correction Δ in [mN/m] is given by the following relationships for the short and medium time intervals (for longer times no correction is needed):

$$\Delta = (-0.44 - 0.26 \ln t_1)(0.8 + \ln \eta) \text{ for } 2.10-4 \text{ s} \le t_l \le 0.1 \text{ s}$$
(10)

$$\Delta = -0.085 \ln t_1 (0.7 + \ln \eta) \text{ for } 0.1 \text{ s} \le t_1 \le 1 \text{ s}$$
(11)

For example, when $\eta = 10 \text{ mm}^2/\text{s}$ and $t_i = 0.01 \text{ s}$ we obtain $\Delta = 2.3 \text{ mN/m}$, and for $t_i = 0.1 \text{ s}$ the correction reads $\Delta = 0.5 \text{ mN/m}$. For pure water and aqueous solutions corrections of $\Delta = 1.1 \text{ mN/m}$ at $t_i = 0.001 \text{ s}$ and $\Delta = 0.1 \text{ mN/m}$ at $t_i = 0.1 \text{ s}$ are obtained. Note, instruments of other producers neglect the viscosity effect via calibration. This works only, however, when the calibration is done with a liquid of respective viscosity. For capillaries of other diameter the correction equations will change.

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Main Features of the BPA-1P

- direct precise measurement of deadtime and life time
- representation of results in function of physical time as well effective adsorption time
- broad available time interval of 4 orders of magnitude
- precise measurement of dynamic surface tension
- direct measurement of hydrostatic pressure
- correction of gravitation and viscosity of the liquid
- temperature control of the sample

Fields of Application

- surfactant science
- ink jet printing
- coating technology
- foam and emulsion technology
- detergency
- pharmacy, cosmetics, food technology
- medicine and biology
- ecology

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Main technical data BPA-1P

Surface tension range	10 – 100 mN/m
Reproducibility of measured values	± 0.1 mN/m
Accuracy of surface tension	± 0.25 mN/m
Dynamic time range	10 ms – 10 s
Min. volume test liquid	1 ml
Temperature range	0 90 °C
Experimental time:	
Standard modus	20 – 35 min
Fast modus	4-6 min
Power requirements:	
Measurement Unit	12 VDC
Power Supply	100–250 VAC, 50-60 Hz
Max. Power Consumption	1 Watt
Battery	3 h
Dimensions:	
Measurement Unit (W x D x H)	170 x 110 x 70 mm
Tripod (W x D x H)	150 x 180 x 300 mm
Weight:	
Measuring unit	1 kg
Tripod	2 kg
Interfaces:	RS-232 (standard)
	Infrared (optional)
Max number of measurement point saved in each	50
measurement unit	

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The obvious advantages of the BPA-1P are:

1. Direct measurement of the hydrostatic pressure

In the BPA-1P, a single capillary is employed. To determine the hydrostatic pressure exactly, the liquid/gas interface is automatically searched, and then the capillary is subsequently immersed to a depth chosen by the user (2 to 20 mm, with an accuracy of \pm 0.1 mm). Some commercially available devices employ a second capillary to compensate for the hydrostatic pressure. However, for surfactant solutions this method is less precise than for pure liquids, for which it was proposed (S. Sugden, J. Chem. Soc., 121(1922)858).

2. Correction for the gravitational effect

The BPA-1P employs stainless steel capillaries with various diameters (0.25 to 1.0 mm). The calculation of surface tension from the measured pressure value via the Laplace equation automatically corrects for the non-sphericity of the bubble caused by gravity. Other known devices are only calibrated with a respective liquid of known surface tension. This procedure (also available in the BPA-1P) is unable to compensate the gravitation effect for the whole range of measured surface tensions because the correction depends on surface tension.

3. Direct precise measurements of dead time and lifetime values

The BPA-1P provides explicit measurement of the time interval between two bubbles t_b , the dead time t_d and the lifetime t_l . These characteristic bubble times are determined from the analysis of oscillations of air flow fed into the system. In bubble pressure tensiometers of other producers, the pressure oscillations are used to

determine these time values, which results in errors in the lifetime determination which are several times larger than those for the flow oscillations implemented in the BPA-1P, especially at high frequencies of bubble formation.

This way of determination of characteristic bubble times is subject of a patent.



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4. Representation of results as dependence on effective time

The user has the option to recalculate the measured lifetime values into the so-called effective time, i.e., the time which corresponds to a respective non-deformed bubble surface. This enables the comparison between BPA-1P data and those obtained from theoretical models and values obtained by other methods which either do not involve any surface deformation (bubble or drop shape method, ring or plate methods etc.), or involve a surface deformation following other laws, such as the drop volume method (see DVA-1).

5. Choice of reasonable capillary parameters

The BPA-1P device provides an option to vary the dead time within a wide range. This is made possible due to an additional aerodynamic resistor located between the capillary and measuring system, and also due to the presence of the bubble deflector which can be installed at the capillary tip. Depending on the type of the studied liquid, on the surfactant concentration, and on the specific studies to be performed, the user chooses the combination of the capillary diameter, deflector and the resistor, which yields the necessary dead time value. With these options, the dead time can be varied in the range of 10 to 100 ms. The higher the solution concentration is, the shorter should be the dead time in order to obtain reliable surface tension values in the surface lifetime range of milliseconds. Tensiometers of other producers do not account for the effect of the solution concentration on the capillary geometry (*V.I. Kovalchuk and S.S. Dukhin, Colloids & Surfaces A, 192(2001)131*).

6. Constant pressure in the system to the pressure within the bubble

In the BPA-1P tensiometer the high ratio of the measuring system volume to the volume of one separating bubble is maintained (3000-5000, as it is the case in earlier versions, such as in the MPT2 of LAUDA). This ensures that the pressure in the measuring system is equal to that in the bubble at the time moment of maximum pressure (within better than 0.1 %). Other tensiometers are characterised by a significantly lower volume ratio, which leads to systematic errors.

7. Precise calibration of the device

In the BPA-1P, also a calibration with a liquid of known surface tension is implemented. The calibration is performed in the time range between 0.5 to 1.0 s.

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This results in less stringent requirements regarding the presence of surface active impurities in the calibration liquid. For example, the addition of a surfactant to water with a concentration of 10^{-5} mol/l or lower would not affect the surface tension in this time range. For precise measurement the BPA-1P provides an automatic account for the aero-hydrodynamic resistance of the capillary. Therefore, the measured value of surface tension for pure liquids remains constant (to within 0.1 mN/m) throughout the entire range of measurement time.

8. Automatic correction for the viscosity of liquid

The user has two options to introduce the correction for the viscosity of the studied liquid. In the first (precise) one, the viscosity is considered to be the known parameter of the system studied. In this case, the BPA-1P measuring program employs the procedure which accounts for an additional hydrodynamic resistance at short bubble lifetimes according to the Stokes' law. Also, the approximate automatic procedure is provided, based on the correlation between the viscosity and dead time values (*V.B. Fainerman, A.V. Makievski and R. Miller, Colloids Surfaces , 75(1993)229*). This procedure is efficient for liquids with viscosity 2 to 50 times higher than that of water. In these cases, the user does not need to entry the viscosity value among other parameters of the studied system.

9. Option to perform measurements with small volumes of studied liquid

The standard volume of the studied liquid is 20-25 ml. However, for the use in biological and medical studies, the BPA-1P tensiometer can be equipped by a special measuring cell, for which the volume of studied liquid is 1 ml, see Figure.

A special measuring program is provided for the experiments with such small volume of the studied liquid at minimum foam formation. This enables the application of the BPA-1P device in medical studies for measurements of dynamic surface tension of human liquids:, such as blood serum, urine, amniotic and cerebrospinal liquid, bile etc.



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10. Precise measurements of the dynamic surface tension

The adjusting procedures implemented in the BPA-1P tensiometer, the reasonable choice of the geometry of capillary and measuring system make it possible to measure the dynamic surface tension with an error smaller than 0.25%. The reproducibility of the results is even better than \pm 0.1 mN/m. The error of surface tension measurements claimed for other commercially available MBP devices is also of the order of \pm 0.1 mN/m. This value is, however, misleading as it refers to the pressure measurements only. At the same time, to determine the surface tension from the measured pressure value, one has to account for the hydrostatic pressure, to introduce the correction for the gravity effect, the aerodynamic resistance of the capillary and the viscosity of the studied liquid. It is also important to employ the correct relations between bubble volume and volume of the measuring system, and between the dead time and the concentration of the studied solution. No device, as far as we are aware of, makes full account for all these factors and criteria. If these factors are not considered large errors in the dynamic surface tension of 10 mN/m and more can result.

11. Wide variety of measuring regimes

The user can choose between various regimes of the dynamic surface tension measurements:

- the set of certain number of points (5 to 50) in the predefined lifetime range (10 ms to 10 s) with the averaging over 5-10 measurements and the calculation of standard deviation; the time dependence of the surface pressure can be represented in the natural, logarithmic or exponential coordinates;
- rapid scanning for several (2 to 5) chosen values of lifetime with predefined periodicity; graphic dependence could be displayed;
- continuous (or with predefined periodicity) measurement for a single lifetime value, with the displaying of the dependence on time.

Last two regimes can be used in the monitoring and automatic process control systems.

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Use of BPA-1P in scientific studies and applications

The BPA-1P is the key device for the studies of dynamic surface tension and adsorption kinetics of surfactants (including low-molecular surface active substances and polymers), the important device in the monitoring of the micelles dissociation kinetics. The BPA-1P is indispensable for the development of efficient compositions of detergents, coatings and dyes, cleaning agents and cosmetic applications, foam and emulsion stabilisers, for the analysis of pharmaceutical preparations.

The example illustrated in the following Figure is the dependence of the dynamic surface tension of the aqueous solution of the cationic surfactant CTAB on the effective time in the range of 10 ms to 10 s for the concentrations 0.2, 0.5 and 1.0 mmol/l without the addition of NaCl (open symbols) and with the addition of 0.01 M NaCl (closed symbols).



Dynamic surface tension of the cationic surfactant CTAB

Dynamic surface tension of the ionic surfactant CTAB with 0.01 M NaCl (closed symbols) and without NaCl (open symbols)

It is seen that with the increase in the CTAB concentration the decrease of the equilibrium surface tension takes place, while the dynamic surface tension approaches the equilibrium value more rapidly. At the same time, the effect of the

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NaCl addition is different for different CTAB concentrations: for the concentrations of 0.2 and 0.5 mmol/l the rate of the surface tension decrease becomes higher throughout the entire time range, while at the concentration 1.0 mmol/l the addition of NaCl results in the significant increase of the surface tension in the short time range. This effect can be attributed to the influence of NaCl on the micelle formation in the HTAB solution and to the relative rate of the micelles decay. This example illustrate the fact that it is the dynamic surface tension which should be investigated, because at the equilibrium above 10 s time range for the CTAB concentrations studied) the addition of NaCl did not result in any anomalous behaviour.

The results obtained for the solution of the non-ionic surfactant C_{12} DMPO at different concentrations (0.5, 1.0 and 2.0 mmol/l, two experimental series for each concentration) are shown in the following figure.



Dynamic surface tension of the non-ionic surfactant C₁₂DMPO

Other examples of the application of the maximum bubble pressure tensiometry are presented in the References.

Human biologic liquids (blood serum, urine, synovial and cerebrospinal liquid, bile, gastric juice, saliva etc.) contain various surface-active substances. Their composition depends on the state of the human organism. It was shown in numerous experiments that studies of the dynamic surface tension of these liquids could provide additional information useful for the diagnostics of the diseases and for the

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monitoring of the therapeutic process (*V.N. Kazakov, O.V. Sinyachenko, V.B. Fainerman, U. Pison, R. Miller, Dynamic Surface Tension of Biological Liquids in Medicine, in "Studies in Interface Science", Vol. 8, D. Möbius and R. Miller (Editors), Elsevier, Amsterdam, 2000*). The dynamic tensiograms of saliva taken from 4 healthy males (lower curves) and 4 healthy females (upper curves), age 21-22, are shown in the figure below.



Surface tension of saliva of 8 different patients

The tensiograms of cerebrospinal liquids, blood, urine and gastric juice (corresponding curves from top to bottom) in the next figure show that the highest surface activity is characteristic to the gastric juice. The existence of pathologies affects the shape of the tensiograms essentially.

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Dynamic surface tensions of four different human liquids (for details see text)

The application of BPA-1P in cases of neurological, nephrological, pulmonological, gastroenterological, rheumatologic, oncological, traumatic and other pathologies can be especially efficient. Numerous medical applications of the maximum bubble pressure tensiometry in medicine can be found in the above mentioned book by *Kazakov et al.*

Nominations

- η viscosity [mm²/s]
- $t_{\text{b}} \text{bubble time [s]}$
- t_d deadtime [s]
- t_i bubble lifetime [s]
- $\Delta-$ correction of surface tension [mN/m]
- P measured pressure [Pa]
- r_c radius of capillary [mm]
- $k-\mbox{correction}$ coefficient for the capillary [/]
- ρ density of sample liquid [g/cm³]
- g gravity constant [m/s²]
- h capillary immersion depth [mm]
- γ surface tension [mN/m]
- γ^* corrected surface tension [mN/m]

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Our recent scientific publications on the maximum bubble pressure technique

V.B. Fainerman, R. Miller and A.V. Makievski, Accurate analysis of the bubble formation process in maximum bubble pressure tensiometry, Rev. Sci. Instruments, (2003), submitted

V.B. Fainerman, S.V. Lylyk, A.V. Makievski and R. Miller, Maximum bubble pressure technique to measure dynamic surface tensions of surfactant solutions in the short time range - limits of applicability, Colloids Surfaces A, (2003), submitted

V.B. Fainerman, V.D. Mys, A.V. Makievski and R. Miller, Correction for the aerodynamic resistance and viscosity in maximum bubble pressure tensiometry, Langmuir, (2003), submitted

Ch. Frese, S. Ruppert, M. Sugár, H. Schmidt-Lewerkühne, K.P. Wittern, V.B. Fainerman, R. Eggers and R. Miller, Adsorption kinetics of surfactant mixtures from micellar solutions as studied by maximum bubble pressure technique, J. Colloid Interface Sci., (2003), in press

R. Miller, A.V. Makievski, C. Frese, J. Krägel, E.V. Aksenenko and V.B. Fainerman, Adsorption Kinetics of Surfactant Mixtures at the Aqueous Solution - Air Interface, to be Tenside Surfactants Detergents, 40 (2003)

V.B. Fainerman and R. Miller, Maximum bubble pressure tensiometry – an analysis of experimental constrains, Adv. Colloid Interface Sci. (2003), in press

V.B. Fainerman, A.V. Makievski and R. Miller, Ein neues Blasendrucktensiometer -Messung der Oberflächenspannung im Bereich von Millisekunden bis Minuten, Labor Praxis, (2003), submitted

M. O'Neill, A.V. Makievski, S.A. Zholob, V.B. Fainerman and R. Miller, Dynamic surface tensions of surfactant solutions measured by bubble pressure and bubble shape tensiometry, Seifen- Öle- Fette- Wachse, (2003), submitted

J. Meissner, J. Krägel, C. Frese, S. Rupert, V.B. Fainerman, A.V. Makievski and R. Miller, Comparative studies of the dynamic surface pressure of C₁₂EO₆ solutions, performed using different maximum bubble pressure tensiometers, Seifen - Öle-Fette –Wachse, (2003), submitted