Surface Tension Measurements Using the Drop Shape Method

By Roger P. Woodward, Ph.D.

First Ten Angstroms, 465 Dinwiddie Street, Portsmouth, VA 23704
Tel: 1.757.393.1584 Fax: 1.757.393.3708 email: sales@firsttenangstroms.com

Drop shape analysis is a convenient way to measure surface tension. The principal assumptions are

- The drop is symmetric about a central vertical axis: this means it is irrelevant from which direction the drop is viewed.
- The drop is not in motion in the sense that viscosity or inertia are playing a role in determining its shape: this means that surface (or interfacial) tension and gravity are the only forces shaping the drop.

The two principal practical advantages of the technique are

- Calibration is straightforward in that only optical magnification is needed. This can be measured with high accuracy and is easy to trace to national standards. (Density must be known by this and all methods.)
- Solid surfaces of the apparatus involved need not have any special cleanliness because their wettability, per se, does not affect the result. This is a significant advantage over such techniques as the Wilhelmy plate where cleanliness is required.

Surface tension is determined by fitting the shape of the drop (in a captured video image) to the Young-Laplace equation which relates inter-facial tension to drop shape. The software does this automatically.

We will now lead the reader through the process of making real measurements. While we will use the term *surface tension* as a convenience, we recognize all of these measurements can be made on a *liquid-liquid* interface as well as on a *liquid-vapor* interface.

Step 1. Determine Geometry. There are actually four combinations from which to choose:

- Pendant drop hanging down. The pendant drop is the familiar tear-drop shape. In this mode, the drop is the heavier of the two media when forming a liquid-liquid interface.
- Pendant bubble floating up. The dispense tip is now below the bubble and the bubble (drop) is the lighter of the two phases.
- Sessile drop. This is a sitting drop, as in a drop of water resting on a table. The drop is the heavier phase.
- Sessile bubble. The bubble (drop) is floating up against the top of the container and is the lighter phase.

FTÅ instruments can make all four kinds of measurements when equipped with the appropriate chambers or cuvets.

The pendant drop mode is always more accurate than the sessile drop because the assumption of axial symmetry is easier to satisfy. Sessile drop measurements are used when it is not convenient to form a pendant drop. The primary area where this is true is molten materials such as glasses, metals and polymers.

The choice of drop-down or bubble-up is a matter of convenience in liquid-liquid interfacial work if both fluids transmit light, otherwise the outside media must be transparent. In liquid-vapor work, the drop-down mode is always used.

An interesting facet of the Young-Laplace equation is that it *requires* the drop to be distorted by gravity, as it balances this distortion against the restoring force of surface tension. Surface tension can not be determined for a spherical drop, i.e.,

one unaffected by gravity. Therefore the height of the drop must be enough for the pressure difference between the top and bottom to distort the drop. This is ensured by using a dispense tip large enough to support the needed drop size. This may take some trial and error. Lower surface tensions require even larger tips to support the required volume. A 20 gauge needle with an outside diameter of 0.914mm is a good starting place for liquid-vapor work.

Step 2. Setup Instrument. We must next load the liquid in the syringe (or cuvet) and obtain a good video image. Figure 1 shows some choices.

Figure 1. Syringe, cuvet and needles.

This particular syringe is a Hamilton 250µl, but you can choose from 25 to 500µl capacity in this style. The larger syringes offer the convenience of providing many drops, yet still offer good volumetric resolution.

You must tell the software the syringe internal diameter so the pump will be calibrated. This is done on the Pump tab. For the syringe in the figure, the capacity is 0.250ml and the scale's linear length is 60mm, for which the calculator on the tab provides a diameter of 2.303mm.

The round collar at the upper end of the syringe is an adapter for to the pump holder. Different adapters let you use syringes up to 10ml in size.

A disposable cuvet is shown below the syringe. A dispense needle passes through the cuvet top. This allows the cuvet to be used with the needle entering from the top for pendant drop-down measurements, or upside down with the needle entering from the bottom for pendant bubble-up measurements. The total volume inside the cuvet is 4.5ml. Cuvets are a convenient way of protecting pendant drops from air currents and for controlling evaporation. They are a necessity for liquid-liquid work. Optional temperature control stages are available for these cuvets.

The needles shown in Figure 1 are 22 gauge with an outside diameter of 0.71mm. Figure 2 shows a range of choices in disposable needles, including an all-plastic beveled tip (at the bottom) which is useful for low surface tension liquid-vapor measurements when a cuvet is not used. A Luer adapter "extension tube" is also shown in Figure 1. It is used in the inverted mode bubble up mode to connect the syringe to the dispense tip, since the tip is no longer directly under the syringe.

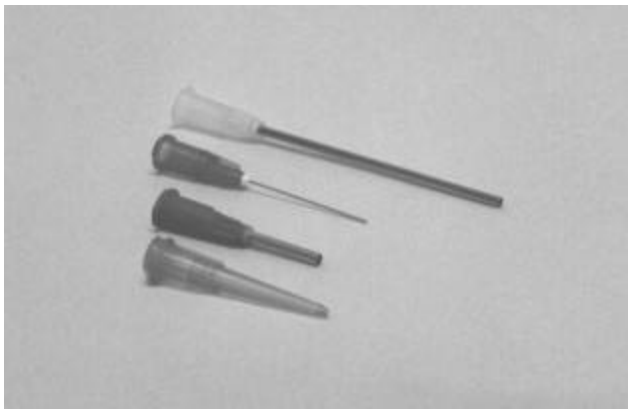

Figure 2. Example needles.

The Help/Reference section in the software contains a listing of needle diameters.

Most of the time we will load fluid in the syringe (but not always, because you can perform a liquid-vapor measurement in a bubble-up mode with the syringe controlling the vapor bubble). If you wish to fill a small syringe, the best way is to use a *second* syringe. Fill it in the normal way by drawing fluid up through its attached needle. Then dispense this into the first syringe with its needle removed and the syringe held upside down. In this fashion fluid flows down into the syringe and, if one is careful, will displace all of the air. Once the small syringe is absolutely full, attach the needle. Now you may turn the syringe over if you wish. Dispense enough fluid to displace the

air in the needle. This is one reason to use a larger capacity syringe, because the needle body will hold 25µl or so and this will use up most of a, say, 50µl syringe.

If you wish to use only a very small amount of fluid sample, you will not want to fill the syringe. Instead, you may leave air in the syringe and draw only a small amount of fluid up into the needle body. It is practical to make measurements with at little as 20µl total fluid in this fashion. (You need to keep some fluid in the needle while the drop is formed, so, for example, 20µl would support a 10µl drop.)

A more sophisticated alternative to this is to fill the syringe with a *working fluid*, but keep an airgap between it and the fluid being tested. Fill the syringe as before, but expel air from only the visible part of the Luer hub (generally you can see into the plastic hub on these needles). Then draw test fluid up into the needle portion. Use the syringe scale to precisely draw, say, 20µl. Experiment to see how much you can pick up without the test fluid infringing on the area previously wetted by the working fluid.

Mount the syringe and, if used, the cuvet and obtain a video image of the needle tip. Align the camera so its line-of-sight is exactly horizontal and the dispense tip is in focus.

Step 3. Magnification Calibration. This is an iterative process, because we must know how large the drop is going to be before setting magnification, and we can't calibrate until magnification is set.

Form a nicely shaped pendant drop and take a Snap Shot. Adjust the magnification so the drop occupies about 75% of the vertical height of the image. ***This is most important! Small drops do not provide enough pixels for good accuracy.***

Measure surface tension by clicking on Surf Ten in the movie. Roughly calibrate magnification on the Calibration tab using the Measured Tip Width from the Surface Tension tab and the manufacturer's diameter for the needle from Help/ Reference. Next you must measure a standard. You may use a known fluid or a mechanical standard. The latter is often preferable, because fluids can become contaminated. However, the mechanical standard must fit in the image and requires external measurement to one micron accuracy. A sapphire ball standard is furnished and another choice is the dispense needle. If you use the needle, be sure to measure it at its very tip. The sapphire ball is preferred because it is larger and refracts light like fluids. Take a movie and average the standard. Enter the known and measured values on the Calibration tab. Click Apply.

To obtain the best results, the image must be in precise focus. Ensure the backlight is centered on the drop so the "bright" spot in the drop is square with its maximum diameter. Figures 3 and 4 show images of good size and focus.

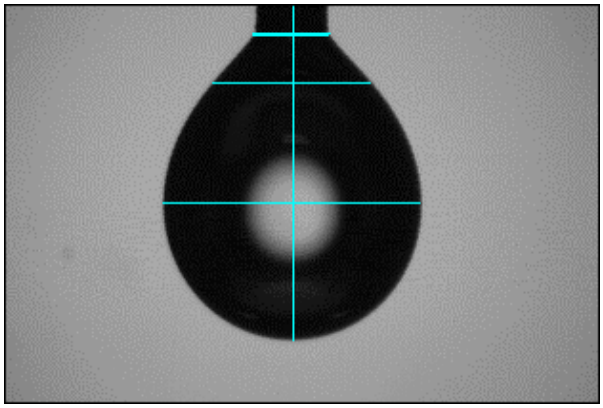

Figure 3. Pendant drop image.

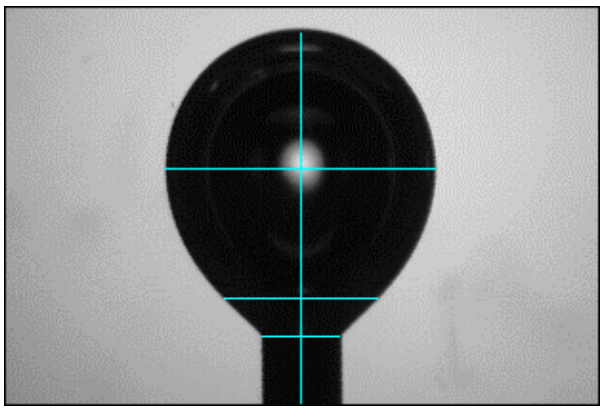

Figure 4. Pendant bubble image.

The software automatically places graphics over the drop image for quality assurance. The vertical line should fall in the center of the drop to assure axial symmetry. There is a horizontal line at the maximum diameter; it should terminate on the edges. If drop volume and surface area are computed, a horizontal line is drawn at the wetted end of the tip where the fluid volume and area measurement terminate. This line can be placed manually by selecting Manual Angle Baseline on the Surface Tension tab. Then click Angle and use right mouse clicks to set the baseline. The intermediate horizontal line should not infringe on the tip area; if it does the drop is too spherical.

Focus is extremely important because the drop may move slightly from vibration and, if it then becomes out-of-focus, the drop's edges will be incorrect. The correct procedure is to focus the pendant drop for best clarity with the microscope aperture open and then close the aperture half way or more to obtain greater depth of field. The magnification standard must be measured with the same lighting and aperture setting as the drop.

The following table shows representative Measured Tip Width data for 6 images of a needle measured to be 0.710mm by a micrometer.

0.71104mm	0.70989mm	0.70941mm
0.71017mm	0.70970mm	0.71203mm

Typical standard deviation over a large set will be ≈2μm. Deviations are caused by electronic noise in the image capture, anything adhering to the needle tip, and mechanical vibration. Make sure the tip is visible in the image and is clean. Short vertical lines are drawn where the tip width is measured; these should not infringe on the drop.

Step 4. Long Duration Test.

The next step is to take a movie over a relatively long time to ensure stability. This is to verify technique on initial setup.

You may or may not know if surfactants are present in the fluid. If they are, you expect a time variation in surface tension with interface age; otherwise you expect a stable measurement with only variations from "noise." Noise will set the resolution limit of the system, i.e., the smallest change in value which can be reliably detected. Resolution and accuracy are different: accuracy is the deviation from the "true" value whereas resolution is the noise limit in the measurement. In the drop shape method, accuracy is set by knowledge of magnification and fluid density. Resolution is set by electronic noise and mechanical vibration of the drop.

Figure 5 shows the effects of a dispense needle contaminated by skin oils after being touched. The fluid is water. The initial surface tension after the drop is formed is what we expect (73), but the large molecules adsorb (collect) at the interface and reduce the surface tension. That it takes 30 minutes to do this is not uncommon.

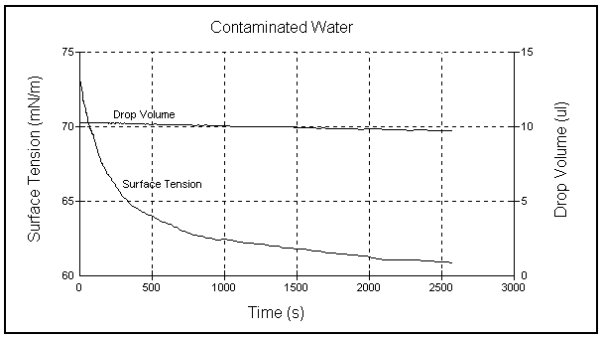

Figure 5. Surfactant adsorbing on surface.

Note also that the volume decreases slightly in time from evaporation, by about 1/2μl. This drop was created just after the needle was placed into the cuvet. Even though the bottom of the cuvet contained water to create a vapor pressure, the atmosphere in the cuvet did not saturate for some time; this allowed some evaporation to take place. This small amount of evaporation is not a problem (it did not affect surface tension), but evaporation should be checked carefully when an enclosed chamber is not used.

The results of the run in Figure 5 were unexpected by the operator, so it is wise to make this kind of check. Figure 6 shows a similar run on the a clean needle.

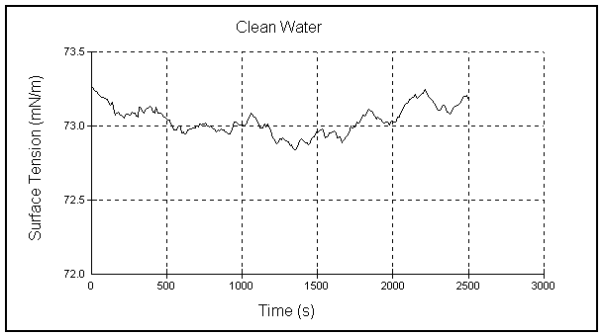

Figure 6. Clean water and needle.

Magnification was calibrated against the micrometer measurement of the needle diameter. The mean μ is 73.0mN/m, the standard deviation σ is 0.100mN/m and COV, the coefficient of variance, is 0.136%. This can be considered good data. The variation which is present is the electronic and mechanical noise in the system.

Step 5. Variance Reduction. The data of Figure 6 is replotted in Figure 7 with the Y axis starting at 0 (i.e., no longer using an expanded scale). It now looks noise-free, but this simply illustrates the importance of the plot scale.

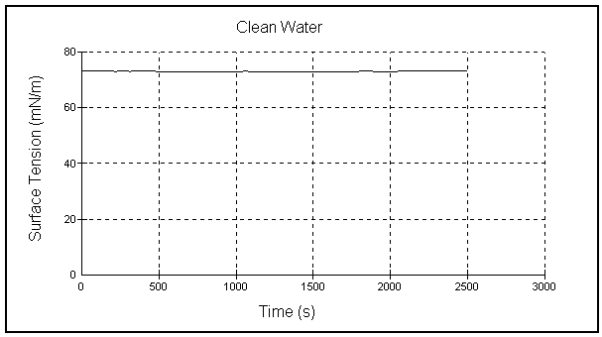

Figure 7. Clean water and needle.

Replotting did not make the data any less noisy, but a reasonable question is "What can I do to reduce noise or variance?" A sequence of experiments using water as the test fluid showed the following variances:

Aperture	Isolation	Filter	COV
1=Open	None	None	0.78%
1/4	None	None	0.32%
1/4	Foam	None	0.21%
1/4	Foam	10 Frames	0.06%

The open aperture data shows the consequence of vibration acting on a small depth of focus. The drop moves in and out of focus and this has a profound affect on the perceived location of the drop edge. Closing the aperture somewhat increases the depth of focus and keeps the drop in focus in spite of small movements, reducing the COV to 0.32%.

The next step is to isolate the chassis. This can be with an airtable or with suitable density foam supporting a heavy plate on which the instrument then rests. In more severe cases, say when the instrument is not on the ground floor, an airtable is recommended. This reduced the COV to 0.21%.

The final step was to employ filtering (averaging) of the data. The filter risetime was set to 10 frame times in Graph Options. For example, since the acquisition period was 0.1s, the filter rise time was set to 1.0s. The filtering time can be adjusted higher or lower, but *some* filtering is most useful.

One advantage of larger dispense tips is that there is greater dampening of vibrations because there is relatively greater adhesion length on the tip compared to the drop mass. This reduces the effects of mechanical noise.

Step 6. Special Cases. When you pump more viscous fluids, the pumping rate must be slowed to accommodate the pressure drop across the needle. Unless you have specific need to form the drop most rapidly, pump at 1µl/s or less. If fluid keeps coming after the pump is stopped, this is a sign the pump rate is too high. Glass syringes are better in this regard than plastic ones, because they stretch less under pressure.

Make sure the syringe plunger is firmly attached to the push plate using the clip provided (do not leave it off).

There are many benefits to using glass syringes, even though you must clean them thoroughly after use to prevent cross-contamination from one sample to another. If contamination is a problem, consider loading only the needle and hub, without drawing test fluid into the syringe body. Then the needle itself can be discarded after use.

Another possibility to keep in mind is the "inverted" experiment with the bubble up into the test fluid. This option is available if the fluid is transparent. Fluid never reaches the syringe.

Finally, there are times the sessile drop approach is most convenient. Figure 8 illustrates this with water as the test fluid.

If you must deal with molten materials, and particularly if they must be heated to temperatures beyond what your instrument chamber can handle, consider photographing them with 35mm slide film (it is dimensionally stable). The slide can then be analyzed by the FTÅ instrument.

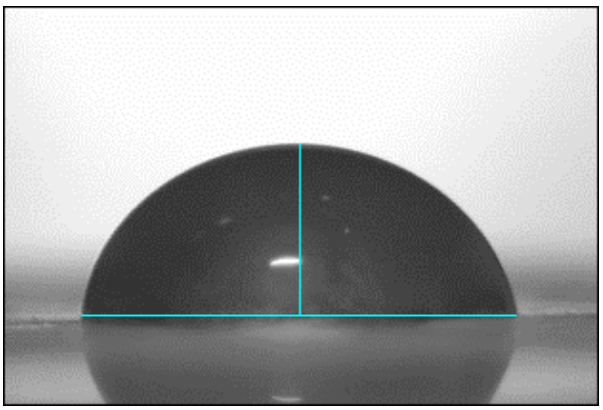

Figure 8. Sessile drop surface tension.

Useful Relationships. The shape of a drop is determined by its radii of curvature, R_1 and R_2. In the case of a spherical drop, these are equal. For precise geometric definitions of these radii, see the references cited below (e.g., Adamson). The relationship between interfacial pressure (the pressure across the interface) and these radii of curvature is called the Young-Laplace equation:

$$\Delta P = \gamma (1/R_1 + 1/R_2)$$

where

ΔP = interfacial pressure difference
γ = interfacial tension
R_1, R_2 = surface's radii of curvature

In a column of fluid of density ρ and height h,
$\Delta P = \rho g h$

and g is the acceleration due to gravity, ($9.8 m/s^2$).

Among other things, the Young-Laplace equation shows the pressure is quite high in a small drop (e.g., radius of 5 microns).

The volume (or, more correctly, the weight) of a pendant drop that can be supported on a round tip is described by Tate's Law:

$$W = 2 \pi r \gamma$$

where

W = weight of drop
R = radius of wetted tip
γ = surface tension

References.

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- *CRC Handbook of Chemistry and Physics*, ISBN 0-8493-0566-7
- *Physical Chemistry of Surfaces*, Arthur Adamson, ISBN 0-471-61019-4
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- *Contact Angle, Wettability, and Adhesion*, K. L. Mittal, ISBN 90-6764-157-X
- *Wettability*, Berg, ISBN 0-8247-9046-4