FTÅ200 Measurement Capabilities

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The FTÅ200 is an instrument for measuring phenomena such as surface tension, surface energy, and absorption. It is built around rapid video capture of images and automatic image analysis.

Measurement Processes

Measurements are made by observing the drop shape of a fluid which reveals information about the fluid itself or about the surrounding media. In some experiments, the fluid will be the known quantity and the media the unknown being explored, and in other cases these roles will be reversed.

Dispensing. In general, drop volume is quite small, in the range 1–15µl. Sometimes small volumes are only a matter of convenience, but in other experiments small volumes permit better spatial resolution and sometimes they are used to avoid distortions due to gravity. The FTÅ200 uses a highly accurate syringe pump driven by a stepper motor to dispense the test drops. The pump may also be run in reverse to aspirate, or pick up, a drop. It may be used with a variety of commercially available syringes (glass or plastic) and dispensing needles (stainless steel or Teflon-coated).

Image Acquisition. Once there is a drop to observe, images are captured by the computer and stored in memory. A single image may be captured (a snapshot) or a sequence may be captured (a movie). Normally, the FTÅ200 captures images and analyzes them after they have been stored. However, the “real-time” mode analyzes images on-the-fly. This option is somewhat less flexible because the images are not preserved, although the results are stored in a disk file. The image analysis algorithms employed by the software seldom take longer than one second per image, so images can be obtained roughly once per second in real time mode.

Figure 1 shows a typical situation in which contact angle is being determined for a fluid on an unknown substrate. Air surrounds the fluid and substrate.

Image Analysis. The FTÅ200 follows one strategy for all image processing: a set of analytic curves are formed which describe the drop, then these expressions are solved for the desired data. This is the heart of drop-shape analysis implemented by the FTA200 software: reduce a gray-scale image to a set of equations describing the drop’s edges.

Figure 2 illustrates the edge finder algorithm that accurately locates an edge from a gray-scale image. A large number of X,Y points are generated in this manner and then a least-squares fit is used to derive the curve equation. An advantage of the least-squares

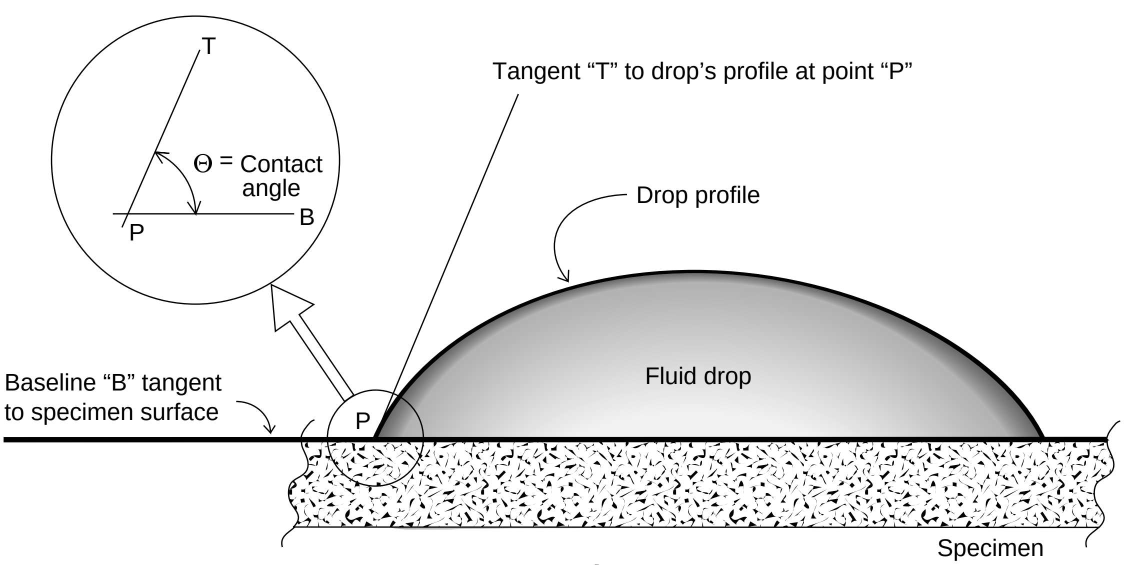


Figure 1. Contact angle measuresment.

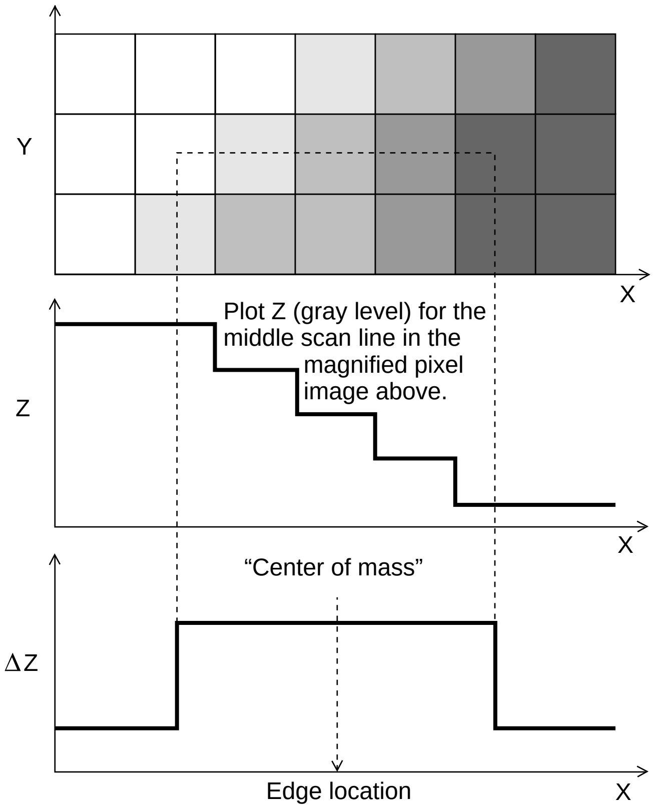


Figure 2. Sub-pixel resolution of the edge finder.

curve fit is that it effectively averages many data points into one equation, thus smoothing the inevitable noise in the video image.

At the top of Figure 2, we see a magnified portion of a gray-scale image edge. Each individual pixel is visible as a block. Only five Z levels of gray are shown; the real images have roughly 250. The graph in the middle shows the gray values as a function of X for a single selected scan line. The bottom graph shows the first differences (or rate of change) of the Z values plotted against X for the same scan line. The "edge" is defined as the centroid of this slope plot. In general, this center of mass will occur at an arbitrary location within a pixel; i.e., the location will be determined with a resolution less than the size of one pixel. This "sub-pixel" resolution allows for great accuracy in the resultant analytic curve. The FTÅ200 measures edges both horizontally, as pictured here, and vertically; then it combines them in an optimal fashion.

The second part of image analysis is to solve the analytic equations for the desired result. In a sense, the edge finder does all the work, because it searches the image for edges and converts them to the coefficients of the desired equations. Once we have the equations, we may solve them in various fashions. The software does all of the following automatically.

For contact angle, it obtains the intersections of the baseline with the drop profile by solving the equations simultaneously. At each intersection point it obtains the slopes by differentiating the equations. Next the arctangents of the slopes are taken to obtain angles. The difference between the baseline angle and the drop profile angle is the contact angle.

For other analyses, the software can solve the equations for distance and area, or it might solve the Laplace-Young equation for surface tension. All solutions are obtained automatically by the software.

The FTÅ200 software also offers unique hybrid image analysis where the user points and clicks on certain features of the image to define some of the lines. The software will take what the user has provided, determine the remainder automatically, and then proceed with solving the equations. This facilitates automatic analysis of complicated or unclear images. In particular, a long movie of complex images can often be analyzed automatically with the operator intervening only on the first frame. Subsequent frames will be analyzed as perturbations of the first. In all of these cases, the operator's input is limited to locating the edges in the image. The software then fits these edges to analytic expressions and proceeds with the same equation solution process in all cases.

Data Reporting. After the images have been analyzed the software provides a variety of editing, smoothing, graphing, and statistical reporting capabilities. Data can be exported to other Windows™ programs or to industry-standard spreadsheets and databases.

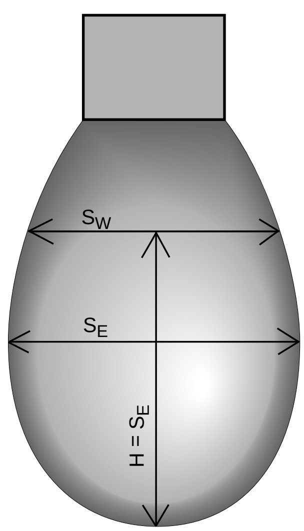
Movie Capture. The FTÅ200 is a dynamic system in that it can capture motion and analyze non-static situations. It has extremely fast image capture—60 independent frames per second, but it can also run slower. It can capture long high speed movies, typically 150 to 300 frames. These movies are stored in the main memory of the computer, which has the advantage of being easily expanded at any time by the user. Slower movies, with frame intervals of a few seconds or more, can be stored directly on the hard disk, in which case there is no practical limit on the number of images in a movie.

The FTÅ200 also has flexible "triggering" capabilities. The trigger sets the reference frame from which other frames are measured. For example, the user may request five frames before the trigger and 25 after. The system keeps a rotating buffer of images; when triggered, it marks the requested number of prior frames for permanent storage and proceeds to acquire the remaining images after the trigger. A trigger may be generated in many ways: manually by the operator, by a fiber optic detector observing the drop, by the syringe pump after a specified volume has been pumped, by a user-set timer, or by external user-provided sensors. Finally, the system has provisions for non-uniform frame periods, so images may be taken rapidly at first and then slowly later on to better match the rapidity of drop shape changes.

Experimental Techniques

Many different parameters can be determined from drop shape analysis. The more commonly used experiments are described below.

Pendant Drop Surface Tension. The Laplace-Young equation[1] describes the shape of a fluid drop under equilibrium conditions. A hanging pendant drop can be analyzed more reliably than can a sitting sessile drop, since one can safely assume axial symmetry for the pendant drop but not for the sessile drop. Figure 3 illustrates a pendant drop and the Bashforth-Adams technique for solving the Laplace-Young equation.



Surface tension is derived from drop shape. Given fluid density, the value of S_W / S_E is an entry into a lookup table which yields surface tension.

Figure 3. Pendant drop surface tension measured by the Bashforth-Adams technique.

Unfortunately, the Laplace-Young equation can not be solved analytically in the general case. Therefore, all solution methods rely on numerical techniques and interpolations. The classic solution was provided by Bashforth and Adams. When done manually, as with a ruler on a photograph, it suffers from the difficulty in finding S_E, the equatorial diameter, because many points have to be measured to determine the true maximum width. When done automatically, it suffers from errors introduced by noise at the specific measurement points. The FTÅ200 extends this technique by optimally fitting curves to the regions of interest in the pendant drop in order to minimize noise effects. The various distances are then determined by solving the equations analytically. An alternative technique is to determine a drop shape parameter by interpolating the drop shape against a set of reference shapes. After the shape parameter is known, the solution follows the classical Bashforth-Adams technique. Although called Bashforth-Adams, most workers use the more modern recalculated tables of Padday.[2]

Pendant Drop Interfacial Tension. Interfacial tension between two immiscible fluids, at least one of which is clear enough to transmit light, can be determined by exactly the same technique as simple surface tension. One must have an appropriate container to hold the surrounding fluid and the operator must supply the specific gravity of both fluids. First Ten Ångstroms can supply suitable interfacial tension chambers.

Dynamic Surface or Interfacial Tension. Temporal variations in surface tension may be caused by the adsorption of fluid components at the drop surface. For variations on the order a few hundred milliseconds or longer, the pendant drop can be dispensed and the movie taken after the pump stops. Figure 4 on the next page illustrates this type of experiment; time resolution is 0.5 seconds. Surface tension decreases in time as the surfactant adsorbs on the drop's surface (i.e., it moves from being uniformly dispersed in the fluid to being preferentially found at the surface).

An alternative method is to first form a pendant drop and let it come to equilibrium. Then the pump adds a small amount of fluid in a short burst. This causes a stress in the surface of the drop (new drop area is

1. Also known as the equation of capillarity. See A.W. Adamson, *Physical Chemistry of Surfaces*, Wiley, ISBN 0-471-61019-4.

2. J. F. Padday, in *Surface and Colloid Science*, Vol. 1, (E. Matijevic, ed), Wiley, New York, 1969.

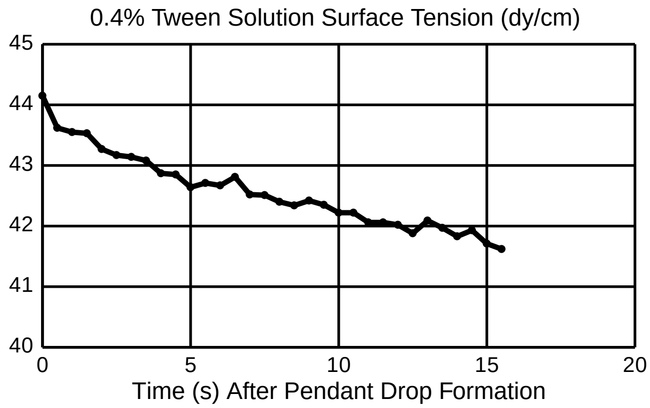


Figure 4. Dynamic surface tension.

formed). If only one motor step is requested, the change is very rapid and is effectively an impulse. The change in surface tension can be measured with 16ms resolution by capturing a movie at the highest speed. Time constants in the 50ms range will have three data points and can be determined with reasonable accuracy using least squares fits. Longer time constants will, naturally, have more data points and higher accuracy.

Contact Angle. Contact angle is probably the most frequently run experiment, as it is used to measure wettability of solid surfaces and can also be used for absorption experiments. The FTÅ200 provides several options for measuring contact angles.

In general, it is easy for the software to find the drop profile, but hard for it to find the baseline. This is because many image defects can obscure the baseline, plus the specimen may be irregular. Conversely, it is easy for an operator to locate a baseline but fitting a tangent to the drop profile is difficult. The FTÅ200 software lets you “mix and match” between operator baselines and software determined drop profiles.

Two kinds of baselines are found in practice. The type of image illustrated in Figure 1 is an idealized one where the camera is looking exactly side-on, with a viewing line parallel to the specimen surface. In many cases, this is not desirable. Often one desires to look down at a slight angle, e.g., two or three degrees. Figure 5 illustrates the two cases for the same drop.

If the drop is not close to the specimen edge, then the downward tilt method will yield a clearer baseline, since the specimen’s front edge cannot be in focus. The baseline is located at the inflection point of the profile between the upper drop image and the lower “reflected” image. The FTÅ200 software lets the user optionally specify a baseline type.

Another option allows the operator to choose between a spherical drop profile fit and a non-spherical fit. The non-spherical mode fits the drop profile only in the regions adjacent to the contact angle point. This is illustrated in Figure 6. The spherical mode fits over the top portion of the drop and down as far as possible towards the contact angle points. Note that it is not necessary for the curve fits to actually reach the contact angle point because the algorithm extrapolates the curves during the process of solving the equations analytically for the intersections. The non-spherical fit is useful when the dispensing needle is left in contact with the drop (for reasons described in a following section) and when the drop is large, and so is distorted by gravity. The spherical fit may be used with smaller drops, and has the advantage that it is more robust against noise in the image.

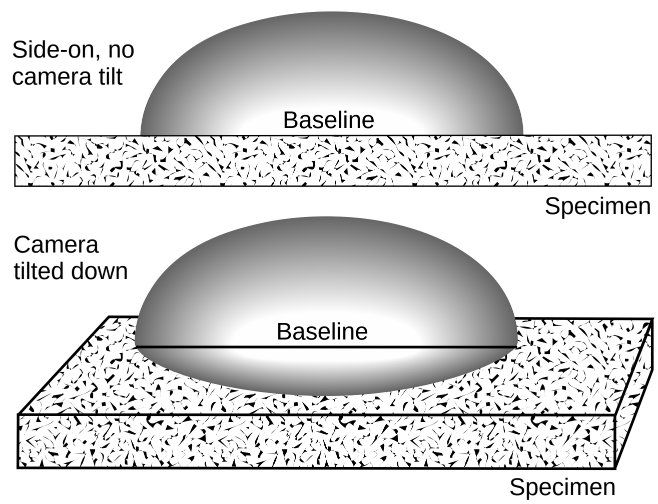


Figure 5. Two possible viewing angles.

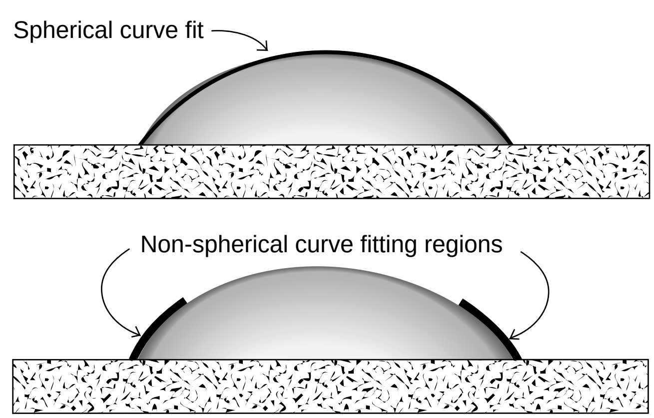


Figure 6. Spherical and non-spherical fitting regions.

Finally, the specimen surface has been assumed to be flat so far. The FTÅ200 has the capability to correct for curved specimen surfaces. The operator measures the specimen curvature, using the FTÅ200 tools, then this curvature is subtracted from the subsequently measured contact angles.

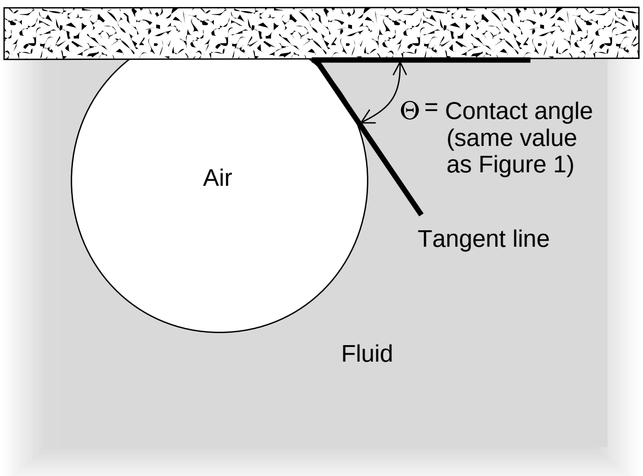


Figure 7. Inverted mode.

Inverted Experiments. Inverted experiments are those in which the surrounding media is the fluid and the "drop" is air, or some other gas. The software will function the same as with normal sessile drops, except the user must specify the inverted mode. Figure 7 shows the geometry in this case. The contact angle is the complement of what would have been the angle in the normal case. The situation depicted in Figure 7 represents the same fluid and substrate as that shown in Figure 1. Note the shape of the "drop" is entirely different.

Advancing Contact Angle. If we keep the needle in contact with the drop and continue dispensing while capturing images, we obtain an "advancing" contact angle. In the laboratory, the contact angle of a properly dispensed static drop, as depicted in previous figures, will be the same as an advancing angle. However, the advancing experiment does have the advantage of covering new territory as the drop expands, so contact angle versus drop width or position data is obtained. This results in averaged data for the overall surface, which is useful since most specimens exhibit variations from point to point. Figure 8 shows the measurement of advancing contact angle. Non-spherical analysis is used to avoid the top of the drop which is distorted by the dispensing needle.

Receding Contact Angle and Hysteresis. Figure 9 illustrates the case in which the pump is reversed and fluid is removed from the drop. The receding mode contact angle will normally be significantly lower than the advancing contact angle.

Contact angles obtained from a combination of measuring advancing and receding angles are sometimes plotted together as shown in Figure 10. The difference between the advancing and receding contact angles is known as the "hysteresis." The FTÅ200 will average the two nominally linear regions and compute the hysteresis. Various explanations are offered for hysteresis based on microscopic compositional heterogeneities or surface roughness of the specimen.[3] Low hysteresis is considered the sign of a "quality" surface in some applications.

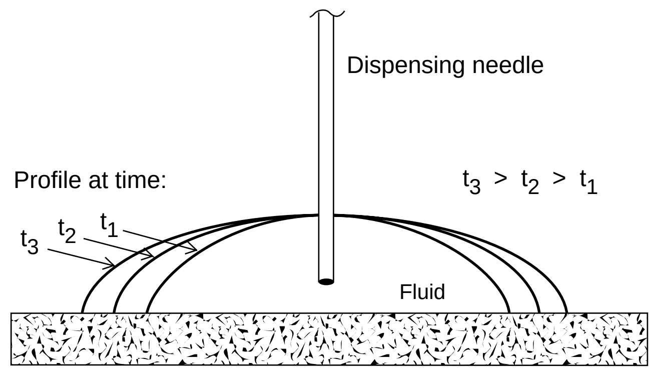


Figure 8. Advancing contact angle.

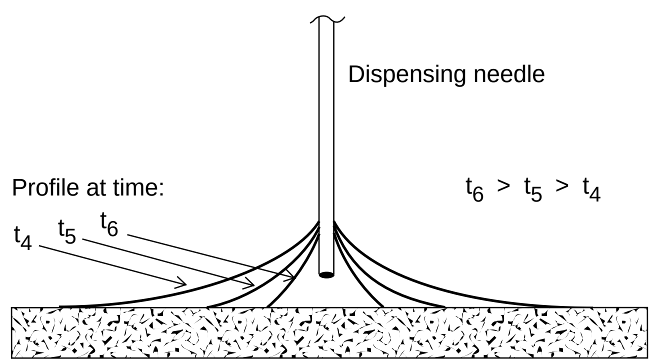


Figure 9. Receding contact angle (continuation of Figure 8).

3. R. E. Johnson and R. H. Dettre, in *Wettability, Surfactant Science Series*, Vol. 49, (J. C. Berg, ed.), Dekker, ISBN 0-8247-9046-4.

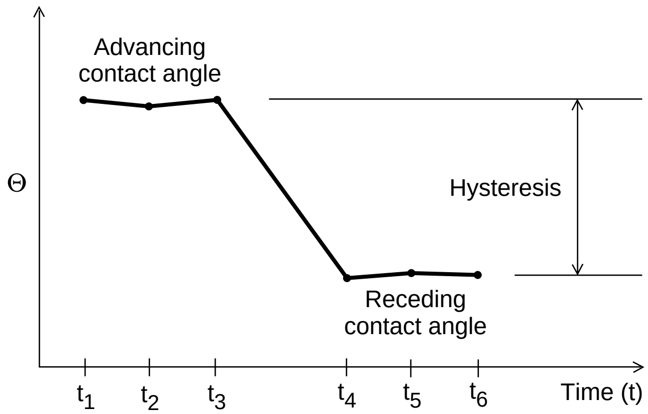


Figure 10. Contact angle hysteresis.

Absorption. Absorbent substrates can be studied with the FTÅ200. A movie is taken of the drop as it absorbs into the specimen. The initial contact angle is often of interest, as is volume of fluid in the drop which is not yet absorbed. A standing volume plot is shown in Figure 11.

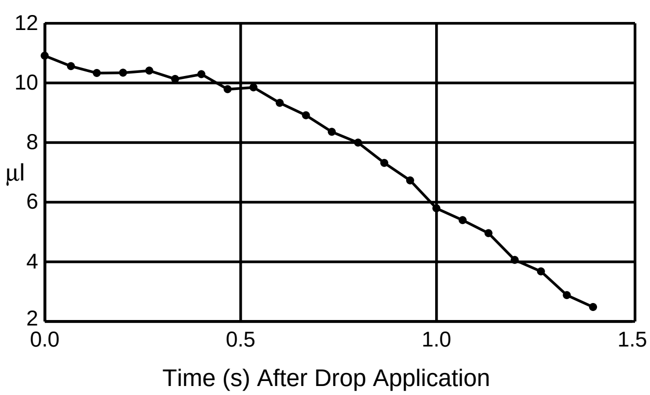


Figure 11. Volume of drop not yet absorbed.

This particular plot shows two regimes, one up to 0.5 seconds and the other after 0.5 seconds. Most likely sizing in the paper was being dissolved during the first half-second, after which absorption could take place more rapidly. The software can also plot base width as a function of time to show spreading, and can compute flow rate into the specimen. These are all derived from the geometry of the drop profile.

Surface Energy Estimates. Whereas the surface tension of a fluid can be determined with accuracy, the same is not true of the corresponding quantity for a solid, surface energy. A solid surface will support a shear stress, whereas a liquid will not support one, so its shape reflects its surface tension. In other words, surface energy remains hidden by the lack of deformability in the solid. However, we can estimate surface energy from the contact angles made by various fluids. Loosely speaking, the more different fluids we use, the better the estimate. Choosing the best fluid(s) is beyond the scope of this discussion (see reference in footnote 3, page 5).

The FTÅ200 provides four models, or equations, for relating contact angles to surface energy. These are solved automatically once the operator has specified the fluids and obtained the contact angles. The simplest, the Girifalco model, is often omitted in other software, yet it is useful in that it only requires one fluid and one contact angle measurement. It is accurate at low contact angles but less accurate at the high contact angles which occur at low surface energies. It can be improved by interpolating, or forcing the answer to be correct for, say, Teflon (data for which is well known). With this improvement, the Girifalco model is useful and convenient in many practical situations.

For more precise work, the software offers the geometric mean and harmonic mean models, both of which require two fluids and two contact angle measurements, and the acid/base model which uses three fluids and three measurements. In all cases, the software reports the components of surface energy appropriate to the chosen model.

Surface Tension from Contact Angle. When it is desired to estimate surface tension for a sessile drop on a known surface, the Girifalco model can run in “reverse,” inputting surface energy and contact angle and calculating surface tension. Along similar lines, the software will predict contact angles given fluid surface tension and substrate surface energy.

Zisman Critical Wetting Tension. The Zisman technique (see reference in footnote 1, page 3) is an alternative to surface energy models. It estimates the fluid surface tension which would just completely wet (i.e., have a zero contact angle) the solid. The estimatation is performed by extrapolating contact angle data from fluids which do not completely wet. Figure 12 shows hypothetical data in a Zisman plot. The vertical axis is the cosine of the contact angle. Noting that the cosine of zero is one, Zisman extrapolated a best fit line through the data and called its tension when the line hit one the *critical wetting tension.* The

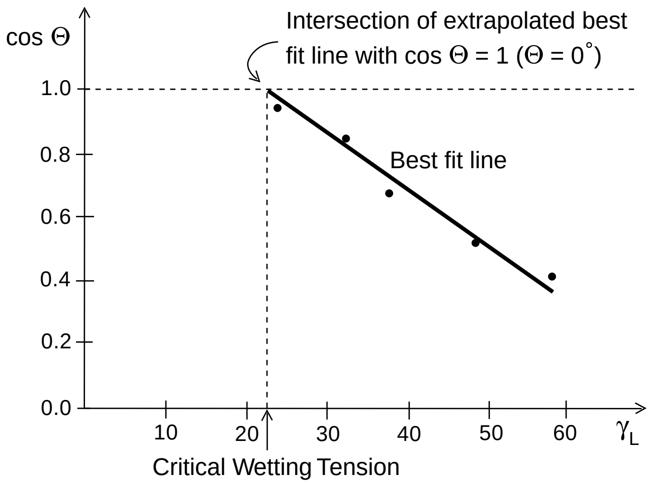


Figure 12. Zisman plot.

FTÅ200 can make this plot and compute the critical wetting tension; the operator measures contact angle with different fluids of appropriate surface tension.

Critical Micelle Concentration. In a fashion similar to the making of a Zisman plot, critical micelle concentration can be determined from surface tension data at various concentrations of the surfactant. Surface tension plotted against log concentration will resemble Figure 13. The operator makes up solutions of known concentrations and uses the FTÅ200 to measure surface tension. This data is plotted by the software and the curve fits obtained. The critical micelle concentration is inferred from the shape of the curve of surface tension plotted against concentration.

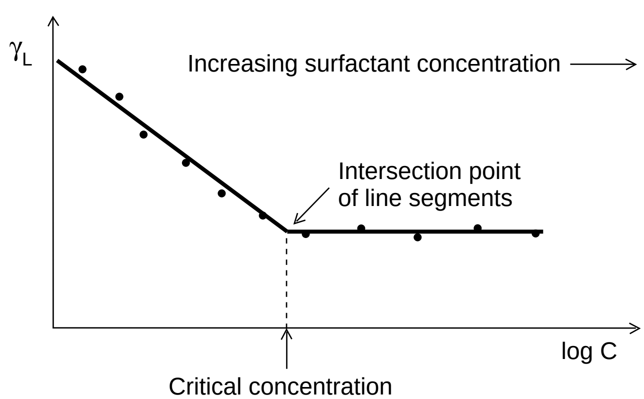


Figure 13. Critical Micelle Concentration.

Hardware Accessories and Additional Techniques

Hardware accessories can be added to the basic system to extend its capabilities and, in some cases, allow specialized measurements.

Robotic Motion. Stepper motor stages are available to position specimens under the dispensing needle. These are available in any combination of X, Y, Z, and rotational stages. These can be used to precisely position samples and to achieve "step and repeat" patterns for analyzing specimen surfaces on a grid. Tilting stages are available for those who prefer this method of obtaining advancing and receding data. The table is tilted until the drop begins to slide "downhill." The downhill contact angle will be the advancing angle and the uphill, or trailing angle, will be the receding contact angle.

Dilution Sequences. An alternative form of the instrument is the Robotic Dilutions System. This configuration uses a valved syringe pump, which is different in that it is placed apart from the dispensing tip and is connected by Teflon tubing. The valve allows the syringe chamber to be connected to either the dispensing tip or a fluid reservoir. The fluid being dispensed need not be the fluid in the syringe chamber; instead an air gap may separate the two in the connecting tubing. The tip is then moved about and positioned by a 3-axis robot while the syringe pump remains fixed.

This instrument can pick up test fluids from a matrix of locations (typically a 96-well plate) and bring them into the measurement position in front of the camera. Surface tension can be measured and a drop can be placed on a test surface for contact angle measurements. The utility of this instrument is that it can be easily programmed to carry out sequences of tip movements, syringe pump operations, and video measurements automatically, all without operator intervention during the sequence. Literally hours of machine operation can be setup in advance. This capability lends itself to the following situations:

1. Dilution Sequences. A dilution sequence involves a large number of fluid samples, progressively more diluted. Sequences can be prepared with as little as 100ul of initial concentrate. Surface tension can be measured as a function of time for each dilution, allowing the calculation of diffusion constants and critical micelle concentrations. Typically dilution sequences are prepared in 96-well plates. The instrument can be programmed to wash the dispensing tip between each sample.

2. Large Numbers of Samples. Instead of preparing dilution sequence samples, the instrument can simply

measure independent samples placed in a 96-well plate or in vials placed on a grid. Again, measurements include surface tension as a function of time and, possibly, contact angle measurements.

3. Multi-Fluid Surface Energy Analysis. With a single-valved syringe pump and the built-in washing protocols, the instrument can place multiple fluids on adjacent locations of a test solid for surface energy determination. This greatly simplifies acid/base surface energy analysis.

3-D Measurements. Another variation of the instrument is the Robotic Mapping System. This system has robotics both for positioning the sample and moving multiple dispense tips. Each dispense tip is connected to a valved syringe pump of the same type used in the Robotic Dilutions System.

These pump/tip combinations can be assigned the tasks of dispensing different fluids (useful in acid/base determinations), or they can be divided between dispensing and picking up drops. This latter is needed for 2-D mapping work, where the first dispense tip deposits drops on specimens for contact angle determination. The second tip then comes along and picks up the drop, leaving the specimen surface relatively free of fluid. This is necessary so previous drops will not interfere with automatic image analysis as new drops are placed on the specimen. The 2-D grid of data is displayed as a 3-D map of surface energy or contact angle on the computer screen.

Environmental Chamber. Environmental chambers provide controlled temperature and atmosphere for the specimen and fluids; often this is useful to maintain a constant relative humidity. These chambers can be electrically heated to 200˚C, and to 300˚C with an optional insulating shroud. They also can be heated and cooled through a fluid loop with an external constant-temperature bath. Temperature control resolution is 0.1˚C and accuracy is a few tenths of a degree. First Ten Ångstroms' chambers are unique in that a specimen positioning slide allows multiple measurements to be taken on a single chamber temperature cycle. While the obvious mode is to bring the chamber to temperature and then make measurements, an alternative mode is to make measurements continuously as temperature is ramped up or down. This obtains surface tension or contact angle as a function of temperature.

Interfacial Tension Chamber. These special chambers are leak and pressure proof and are fluid-loop heated/cooled by an external constant temperature bath. A built-in RTD temperature detector measures the actual chamber temperature which can be used to control a pump on the external bath. As above, the specimen mount has a degree of freedom mechanically for multiple measurements, and temperature may be ramped to obtain experimental data as a function of temperature.

Viscosity Measurement. A simple viscosity determination is possible by measuring the pressure drop across the dispensing needle at a known flow rate. Although not as accurate as conventional viscosity meters, it has the advantage of making the measurement on the same fluid that is used in the surface tension or contact angle work, and it only requires a very small volume of fluid.

FTÅ200 Software Support

First Ten Ångstroms has been shipping Windows™ software since 1994. The software runs equally well on Windows 3.1 or Windows 95. It makes full use of built-in Windows capabilities for printing, networks, and transferring data via the Clipboard to other programs. The software is licensed to instrument customers on a multi-computer basis which means that customers may make copies of the software for other computers they own without charge. This is useful for educational institutions and for users who may wish to analyze data on a separate computer from the one connected to the instrument.

First Ten Ångstroms has a policy of continuously upgrading the software and customers are encouraged to submit suggestions for improvements or extensions. Upgrades are furnished to customers without charge, so there is never a need to requisition more funds to have the latest software.