Comparison of Balance and Drop Shape Techniques

March 12, 2001

The two principal techniques for measuring contact angles are the force balance and the video drop shape method. These are also the principal, but not only, methods for interfacial tension.

Force Balance Method

The FTÅ T10 is a modern force balance. This type of instrument is also known by the names electrobalance and tensiometer, and by the methods it implements, the Wilhelmy plate and Du Nouy ring. The force balance predates the drop shape method as an every-day analytical tool. It measures the vertical force applied to a solid test object by liquid in a vessel. Depending on the arrangement of the experiment, this can be used to determine the liquid's surface tension or the solid's contact angle.

Drop Shape Method

The FTÅ200 is a modern video-based drop shape analyzer. This type of instrument is also called a goniometer, because its historic predecessor used an optical stage called a goniometer to manually determine drop shape, before video cameras and computers were alternatives. The drop shape analyzer directly measures the shape of a small drop using software algorithms. These determine surface tension or contact angle.

Comparisons

Speaking very generally, anything you can measure with one method you can measure with the other. However, often one method is more convenient so both have a place.

The force balance has three primary features: it assumes solid specimens are homogeneous around their periphery, it works only with small samples (<5g), and it works slowly, averaging many readings. These are assets or liabilities, depending on the circumstances. The drop shape method, by contrast, is tolerant of large specimens and those which may not be homogeneous, works very quickly (but does not average), and requires operator care to correctly setup the instrument.

Surface Tension

The force balance offers two techniques for liquid-vapor tension. The Wilhelmy plate dips a platinum plate (≈15mm wide) into a glass vessel containing a moderate amount of unknown liquid (≈10cc or 10ml). The liquid is presumed to wet the plate, which requires the plate to be very clean. The meniscus exerts a force proportional to surface tension and thereby tension is obtained from force and liquid density. The Du Nouy ring dips a platinum ring (≈15mm diameter) into the glass vessel containing the unknown liquid. It then pulls the ring back out, forming what is called a lamella, which is like a meniscus. The maximum force is related to the surface tension. While the ring must be reasonably clean, small imperfections do not affect the result as much as with the Wilhelmy plate.

The drop shape method typically hangs a pendant drop from a small needle and the tension is determined by shape and density. This is very quick and can follow rapid changes in tension from surfactants. Also, the condition of the needle tip does not affect the measurement unless the needle is extremely dirty. On the other hand, the pendant drop is more sensitive to vibration than the force balance. It is easier to correctly setup a force balance for surface tension than drop shape. However the drop shape method can make a measurement with as little as 15µl of fluid, whereas the force balance needs milliliters.

Interfacial Tension

Liquid-liquid interfacial measurements are far easier with pendant drops than force balances because the interface is left undisturbed mechanically. When the ring or plate is inserted into a pair of liquids, one above the other in the force balance vessel, it tends to mix the liquids or one will adhere to the plate. A second advantage the drop shape method has is it can be scaled through magnification and tip size, where there are no analogous parameters for the force balance. Force balance measurements may be useful down to 5mN/m interfaces, whereas drop shape is good down to interfaces like 0.1mN/m.

High Temperature Surface Tension

Polymers, solders, glasses, etc., which are solids at room temperature are more easily measured with the sessile (sitting) drop shape method. No pendant drop is ever formed. Instead, a small clump of sample is heated in a chamber while resting on an inert surface. As the sample melts, it draws up into a drop whose shape is predicted by the Laplace-Young equation for interfacial tension.

Critical Micelle Concentration

CMC's are normally measured with a force balance, particularly when an automatic titrator is employed. The drop shape method requires separate concentrations made by hand and measured separately.

Liquid Density

Density is required by both techniques for all measurements except contact angles by drop shape. The force balance can measure liquid density but the drop shape instrument can not.

Dilational Stress

This form of interfacial rheology (viscosity and elasticity) can be measured by drop shape instruments which perturb the pendant drop volume and continuously measure surface tension. The force balance does not offer this.

Contact Angles

Contact angles on the force balance require small samples which are uniform on all sides. This limits the force balance to studies where the sample can be specially fabricated to fit the instrument. On the other hand, for such studies, the force balance provides excellent averaging of data.

The drop shape method is far more general and can follow faster absoptions than the force balance. It can also work with very large samples and yet provide high spatial resolution for surfaces which are not uniform.

Advancing and Receding Angles

The term "dynamic contact angles" is used in different ways and so is a source of confusion when applied to force balance and drop shape.

The force balance uses the term to mean a moving surface, specifically one which can be slowly moved in both directions so advancing (liquid covering solid surface) and receding (liquid uncovering solid surface) angles are measured. Advancing angles are the largest angles and receding angles are the smallest possible ones for the interface.

The drop shape method naturally produces an advancing angle. Here dynamic means the ability to follow the course of this angle in time, such as when the drop absorbs or spreads. While the drop shape method easily measures an advancing angle, it is difficult to measure a receding angle unless a tilting table is used. The force balance, by comparison, always measures a receding angle along with an advancing angle.

Capillary Measurements

Certain measurements are more easily cast in the form of a capillary rise against a solid surface. The force balance can handle these, as long as the sample is small and uniform, irrespective of whether the contact angle is less than or greater than 90°. The drop shape method only handles less than 90°.

Powders

Contact angles for powders can be obtained through the use of the Washburn equation. The practical way is with the force balance.

Fibers

Contact angles on individual fibers, down to say 10µm diameter, can be measured with the force balance. The capillary rise against larger diameter fibers can be measured with drop shape if the angle is less than 90°.

Accuracy and Resolution

Neither method inherently offers better accuracy than the other when both methods are suitable for the measurement. In these cases, the care in running the experiment, most particularly the cleanliness of the materials, outweighs any instrumental effects. Operator technique, in the sense of sample preparation and the avoidance of contamination, is the main variable since both techniques measure *surfaces* and both can easily detect common contaminates.

Accessories

Both instrument types are often mounted on vibration isolation tables to isolate building noise. This is important when the instrument is on an upper floor.

Circulating baths are used to temperature stabilize specimens with both instrument types. These typically provide control from about 0°C to 150°C. The drop shape method has difficulty below ambient temperature from condensation on chamber windows, often requiring a dry nitrogen flow to clear.

Automatic titrators are used with force balances to automatically determine CMC. Drop shape users must manually dilute their solutions and run individual surface tensions.

Cost of Ownership

The cost of a computer driven force balance will vary from roughly $25,000 to $40,000. Drop shape instruments run from $15,000 to $50,000. Prices vary depending on options and sophistication of the instrument. You can also find some specialty instruments outside these price ranges. Operator training is required on either type, because good lab technique is necessary. The same level of expertise is required as for microscopy.

Representative Instruments

The FTÅ T10 and 200, two example instruments, are illustrated on the following page, along with a summary chart.

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FTÅ T10 Force Balance Tensiometer

FTÅ200 Drop Shape Instrument

Comparison of Force Balance and Drop Shape Methods		
● = best choice; ○ = second best or limited use; x = difficult or not practical		
Measurement	Force Balance	Drop Shape
Surface Tension, Liquid-Vapor		
Pure liquid	●	○
Liquid with surfactant, protein, etc.	○	●
CMC determination, automatic	●	x
CMC determination, manual	●	○
High temperature measurement	x	●
Interfacial Tension, Liquid-Liquid		
Equilibrium interfacial tension	○	●
Dilational stress interfacial tension	x	●
Density of Liquid	●	x
Contact Angles		
Advancing, specially made sample	●	○
Advancing, general industrial part	x	●
Receding, specially made sample	●	○
Receding, general industrial part	x	●
Absorption and spreading	○	●
Fibers, $\theta < 90°$	●	○
Fibers, $\theta > 90°$	●	x
Powders	●	x