Contact Angle Accuracy

29 June 1998

Contact angles are commonly specified in degrees. Of course, the test fluid used in the measurements must be stated, for its surface tension will affect the angle (Young's equation). Contact angles are used to predict wettability and adhesion, and to indicate monolayer coverage of adsorbed or deposited films. Another use of contact angles is to estimate "surface free energy" by using such theories as the Girifalco, Owens-Wendt, Wu, or Lewis Acid/Base models. What is important is that in all of these applications, the variable of interest is proportional or linear *in the cosine of the angle, not the angle itself*. Thus, no matter whether we are measuring the effects of plasma treatment, contamination, thin film deposits, adhesion or whatever, we must ultimately use the cosine of the contact angle. These matters are discussed by Gutowski in Chapter 2 of

Fundamentals of Adhesion, Lee, ISBN 0-306-43470-9

and also in the recent article by Vogler:

"Structure and reactivity of water at biomaterial surfaces," *Advances in Colloid and Interface Science* 74(1998) 69-117

which reviews the entire field of wettability and demonstrates the relevance of wetting tension τ,

$\tau = \gamma_{LV} \cos\theta$

where γ_{LV} is the surface tension of the test fluid and θ is the contact angle.

Now the contact angle θ will vary from 0° with complete wettability to 180° with absolutely no wettability. Cos θ will vary from +1 to -1 as θ varies. As a practical matter, most contact angles fall between 0° (complete wetting, cos θ = +1.00) and 130° (low wettability. cos θ = -0.64). The fact that the cos θ passes through zero is understood and, loosely speaking, is the transition from attraction at high wettability to repulsion at low wettability.

As Gutowski discusses, the range of the cos θ is 2 (from +1 to -1) and we can relate any level of uncertainty in cos θ to uncertainty in θ if we know θ. This is summarized in the following chart. Notice this allowable error in θ varies with θ, being the most stringent at 90°, but errors near zero contact angle are relatively unimportant. The percentage errors reflect the fact that the possible range is 2.

Angle	Degrees for Error in Cosine of Angle =			
	0.01 0.5%	0.02 1%	0.05 2.5%	0.10 5%
θ = 90° cosθ = 0	0.58	1.15	2.86	5.73
θ = 75° θ = 105° |cosθ|=.26	0.59	1.18	2.94	5.59
θ = 60° θ = 120° |cosθ|=.50	0.65	1.31	3.25	6.42
θ = 30° θ = 150° |cosθ|=.86	1.12	2.21	5.31	10.0
θ = 0° θ = 180° |cosθ|=1.0	8.10	11.47	18.2	25.8

Wetting tension τ is a non-controversial method of describing surfaces as an alternative to angle or surface energy. The theories relating contact angle to surface free energy are under attack and

465 Dinwiddie Street • Portsmouth, Virginia 23704 • 1.757.393.1584 Fax: 1.757.393.3708
http://www.firsttenangstroms.com

are likely to be modified in the future. At best, they are engineering approximations. To provide choices, FTÅ software reports all three: contact angle, wetting tension, and surface energy.

Irrespective of how contact angles are measured, whether by the classical Wilhelmy force balance or drop shape analysis of images, good laboratory technique must be applied to obtain accurate results. With force balance systems, good technique is required to know sample dimensions and prevent vibration. With drop shape analysis, good technique is required to have the drop in focus and have a clear baseline

FTÅ instruments offer the user the choice of looking exactly horizontally at the drop (viewing angle of 0°) or looking down slightly (viewing angle of 3°). With the FTÅ200 series, this choice is accomplished by adjusting the camera height and tilt. With the FTÅ100 series, it is accomplished by selecting the prism for the camera (a 93° prism gives a 3° viewing angle). The error introduced by small viewing angles is *not* that of the viewing angle, instead, the error is bounded by (less than) the cosine of the viewing angle, so the factor is 0.998 for 3°. However, the viewing angle *can* have a significant impact of the clarity of the baseline, and baseline errors can introduce contact angle errors of several degrees.

The three example images show a barely acceptable baseline in Fig. 1 (you should be able to do better!), a bad baseline from 3° in Fig. 2, and a clear baseline from 3° in Fig. 3. The baseline of Fig. 1 is on the horizon, which is fuzzy but discernible. This could be improved by better focus or lens aperture setting, in which case the horizon would be sharp. The difference in the last two is that Fig. 2 does not have enough sample surface in front of the drop to create a reflection image, but Fig. 3 does. This 90° test specimen is the most difficult one for automatic baseline determination.

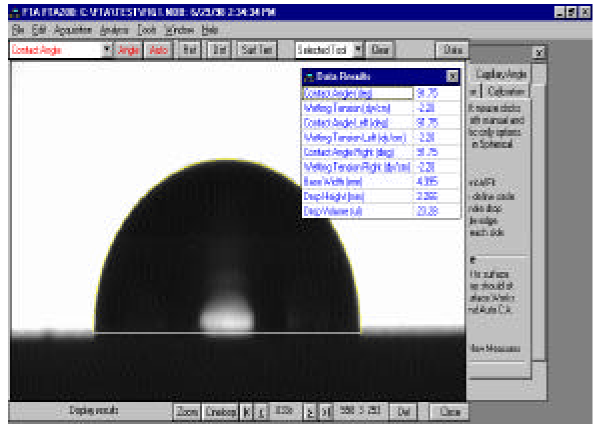

Figure 1. Horizontal view, barely adequate baseline.

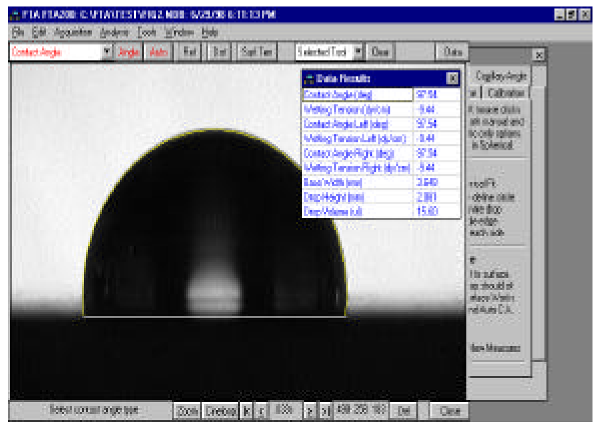

Figure 2. Looking down 3°, bad--unclear baseline.

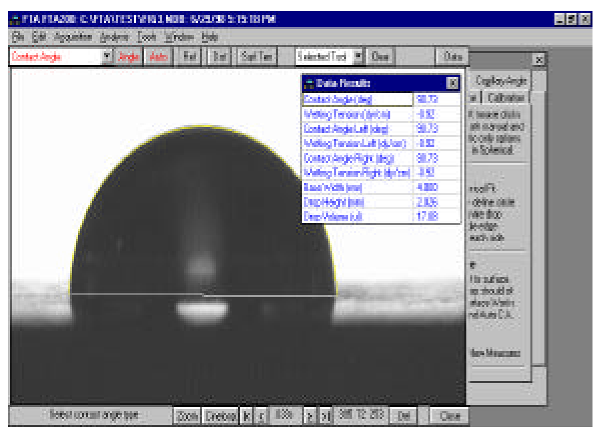

Figure 3. Looking down 3°, good--visible reflection.

The sample in each case was a 4mm sapphire ball embedded in aluminum, so the actual "contact angle" was mechanically known to be 91.1 ±0.3°. The automatically measured values were Fig.1: 91.75° (+0.65°), Fig. 2: 97.54° (baseline low so θ 6.4° high), and Fig.3: 90.73° (-0.37°). Always check the assigned baseline position!