Practical contact angle measurement (4)

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Industry:	**all**
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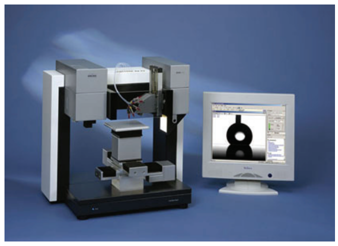
Method:	



Contact Angle Measuring Instrument DSA100

Measuring with method – but with which one?

Keyword: methods, contact angle, sessile drop,

For computer-supported drop shape analysis mathematical models are used which describe the optically determined shape. The DSA software from KRÜSS provides various methods with different application and validity ranges for this. This fourth part on practical contact angle measurement gives an overview of the methods and mentions the criteria for selecting the most suitable method.

The user of the historical goniometer for contact angles was not plagued by the choice of method: by using a scaled rotating disk a tangent was aligned to the drop shape by hand. Today the optical evaluation is carried out by camera and software, which on the one hand represents a great step toward high-resolution and reproducibility, while on the other hand requires more know-how from the user.

Selecting the drop type

Before carrying out the drop shape analysis the *drop type* must be selected in the DSA software. The drop type describes the arrangement of sample and drop in the image. The type to be selected therefore inevitably depends on the measuring setup used.

Sessile Drop

The sessile drop is the standard arrangement for contact angle measurement. A drop lying on the solid surface forms a characteristic contact angle with the surface at the three-phase contact point.

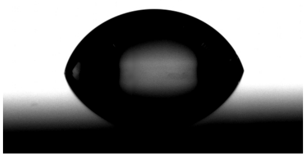


Fig.1: Sessile drop: a drop lying on the solid sample

Captive bubble

With high-energy surfaces the user faces the problem that with each liquid a very small, hardly measurable contact angle is formed. It may also happen that the sample can only be measured when it is immersed in a liquid – soft contact lenses, for example. In such cases the captive bubble method is the classical method: instead of a drop an air bubble is deposited beneath a solid sample surrounded by a liquid phase.

The angle measured within the bubble shape is not yet the contact angle between solid and liquid that we are looking for. This results from the difference between 180° and the bubble angle. The DSA programs carry out this calculation automatically.

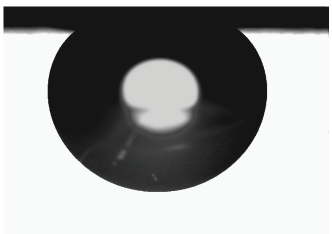


Fig.2: Captive bubble: an air bubble sitting beneath a solid sample

Pendant drop

The pendant drop is not used for contact angle measurements. In this setup a drop (as large as possible) hangs from a needle. If the image scale is known then the pendant drop shape can be used to calculate the surface tension of the liquid.

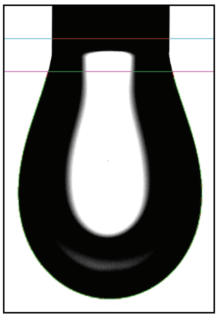


Fig.3: Determining the surface tension on a pendant drop

Shape analysis and baseline

All the KRÜSS drop shape analysis programs determine the contact angle in two steps. In the first step the drop image is subjected to a gray level analysis. The result is an optically determined contour line around the phase boundary in the drop image. In the second step this drop contour is described mathematically. The contact angle is obtained from the angle between this drop contour function and the sample surface, whose projection in the drop image is known as the *baseline* (see Fig. 4).

The mathematical description of the baseline depends on its shape: a straight-line equation for a flat surface, a circular function for rounded substrates.

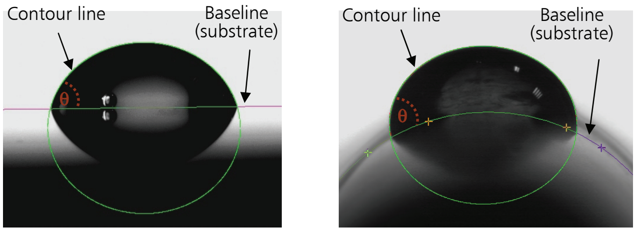


Fig.4 Contour analysis on a flat and a curved sample surface

For the analysis of the drop shape several models are available.

Models for contour analysis

The drop contour is a curved line for whose mathematical description several models are implemented in the KRÜSS drop shape analysis programs (DSA).

The more that the actual contour follows the requirements of the model, the more suitable the model is for analyzing the contour. For this reason the DSA programs show both the optically determined and calculated contour lines. The agreement of these two lines is an important criterion for the quality of the contour analysis.

Circle method

In the *circle method* a drop shape in the form of a circular arc is assumed. This requirement is only fulfilled to a large extent by very small contact angles and drop volumes.

A version of this method is the *height-width method*, in which the height and width of the rectangle enclosing the arc are determined.

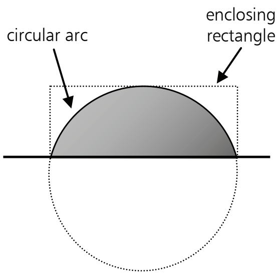


Fig.5 Circular and height-width methods: drop shape as arc

A disadvantage of the height-width method is that instead of the whole contour only a few pixels at the point of inflection and at both sides are used. The measurement is therefore more susceptible to interference in these areas.

Conic section method

In this model an elliptical drop shape is assumed. The *conic section method* or tangent method 1 fits a general conic section equation to the drop shape. The contact angle is determined as the angle between the baseline and the tangent at the conic section curve at the three-phase contact point.

Polynomial method

The *polynomial method* or tangent method 2 only evaluates the phase contact region. Basically there is no geometrical requirement for the contour shape: the polynomial adapts itself to any curve that can be thought of at the three-phase contact point.

Young-Laplace method

The *Young-Laplace fit* is particularly suitable for symmetrical drop shapes that are not affected by interferences such as sample tilting or contact with the deposition needle.

The Young-Laplace method takes the characteristic drop shape under the influence of gravity into account with a sophisticated iteration method. It is also used for determining the surface tension from the shape of a pendant drop (see above).

Choice of a suitable model

The criteria described in this section should help with the selection of the suitable model for the contour fit for the particular drop.

Small or large contact angle?

With small contact angles, particularly in combination with small volumes, the contour can be well described as an arc. For the lower measuring range up to 10° the circle method provides the most accurate results. From about 20° the contour assumes a more and more elliptical shape, which it finally varies from at large contact angles.

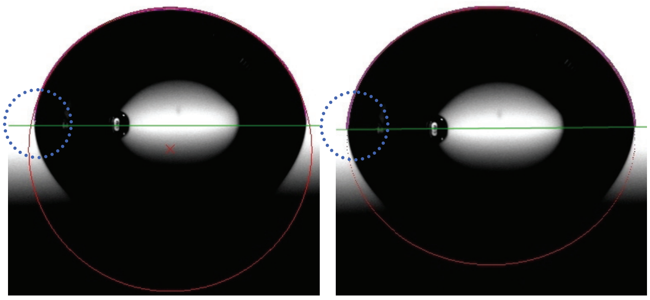


Fig.6: left: circle method, right: conic section method. For the same drop contour the contact angle measured on the left is about 6° too small.

The circle or height-width methods should accordingly only be used for angles up to 20° and the conic section method only up to about 100°. The polynomial method and the Young-Laplace fit can be used throughout the whole measuring range above 10°.

In the captive bubble measurement the angle between the air bubble and the solid is normally very large. For this reason only the polynomial method and the Young-Laplace fit come into question for this method.

Small or large drops?

With larger drops there is also a greater variation of the drop contour from the circular or elliptical shape. Its own weight causes the drop to flatten noticeably. This influence is particularly marked with the test liquid diiodomethane, in which a low surface tension occurs together with a high density. For liquids with such properties the polynomial method or the Young-Laplace fit should be used for drops of more than 3 µl.

Dynamic or static drops?

This criterion is not related to the drop shape itself, but with the deposition method: in measurements using advancing or retreating angles the deposition volume changes continuously; the needle tip is also located within the drop. This means that only methods can be used that are largely insensitive to the contact between drop and needle – the two tangent methods, conic section and polynomial.

In each case care should be taken that the distortion of the drop shape by contact with the needle does not stretch out to the three-phase contact point. This is why larger drop volumes are recommended for measurements with advancing and retreating angles than for static drops. If the adhesion of the liquid to the needle distorts the drop too much then the use of a PTFE deposition needle can provide help.

Symmetrical or asymmetrical drops?

Contact angle measurements are frequently used to study the homogeneity of a sample. If the sample surface is inhomogeneous then it is often not just the contact angles of various drops that differ. Individual drops can also be deformed, so that the contact angles at the left-hand and right-hand sides differ. The same applies to measurements on a tilted table, on which the drops are deformed by the inclination.

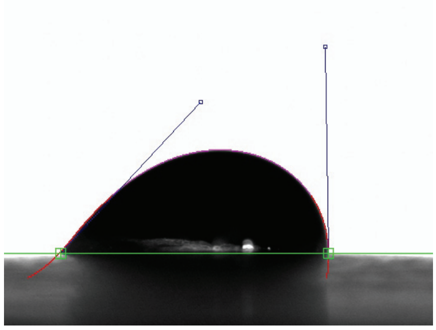


Fig.7: Polynomial fit with a tilted table measurement. The drop shown is located on an inclined surface.

The circle method and Young-Laplace method cannot be used with such drops: they produce a single contact angle which is either inaccurate or completely nonsensical for asymmetrical drops. In such cases only the two tangent methods can be used, as they can detect differences between the left-hand and right-hand contact angles. With very asymmetrical drops only the polynomial method produces reliable values.

Robustness

Up to now it could be assumed that the polynomial method can be used for any shape and size of drop as well as for dynamic drops, so why not always use this method? The answer is that although the polynomial fit can analyze any imaginable curve shape in the contact region, it also reacts to interferences more sensitively than other methods. If the drop image is not flawless, then a "vertical flip" of the tangents can be observed sporadically – the measured angle bears no relationship to the actual value. The polynomial method requires a clean, high-contrast drop shape image to a greater extent than other methods.

The Young-Laplace fit is the model of choice if a symmetrical, disturbance-free drop contour is present - and if the longer calculation time for this fit is acceptable. A symmetrical drop is mathematically represented exactly by the Young-Laplace model, so that the best agreement between the theoretically and optically determined contours can be expected. A further advantage is that if the image scale is known the real drop dimensions – volume and wetted area – can be determined.

Summary

There is no universally suitable model for the drop shape analysis of all shapes and sizes of drops. The size of the contact angle and the drop, the deposition method and the symmetry of the drop are important criteria for selecting the suitable measuring method. The following table provides an overview of the selection guidelines given in this article.

	Circle	Conic section	Poly-nomial	Young-Laplace
Measuring range				
0-20°	✓			
10-100°		✓	✓	✓
100-180°			✓	✓
Drop weight (volume∗density)				
Low	✓	✓	✓	✓
High		✓	✓	✓
Very high			✓	✓
Deposition				
Static (contour without needle)	✓	✓	✓	✓
Dynamic (contour with needle)		✓	✓	
Contour shape				
Symmetrical	✓	✓	✓	✓
Slightly asymmetrical		✓	✓	
Very asymmetrical			✓	