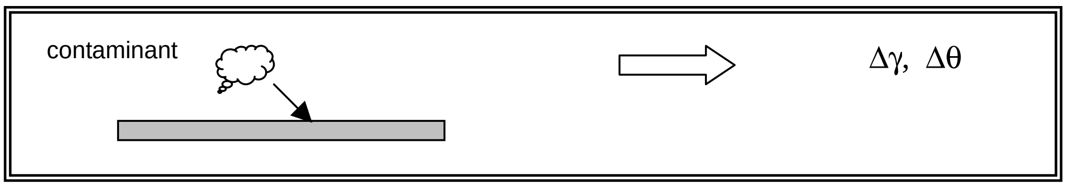
Cleanliness Measurements Using Contact Angles

August 14, 2000

Contact angle measurements can determine the surface energy, γ, of a solid. To accurately measure the surface energy, we must use a set of fluids and the Lewis acid/base theory with the contact angles, θ, for each fluid. However, a simple contact angle measurement with water will give an approximate answer. This is useful because almost all "contaminants" on a surface affect the measured surface energy. This connection



is what we exploit when using contact angles.

Why do contaminants change the contact angle?

Contaminants will change the contact angle if their surface energy is different from that of the clean surface. Since contact angle is a measure of interfacial energy, which is to say the chemistry of the surface, most contaminants will have a different chemistry and different surface energy. While you will want to verify any specific case, this is almost always true.

In what way do contaminants change the contact angle?

Metals and semiconductors ("semi-metals") tend to have high surface energies. Metal and semiconductor oxides have medium to high surface energies also. Grease, oils, hydrocarbons and polymers tend to have low surface energies, on the other hand. Therefore, if our clean substrate is a metal or semiconductor, we expect hydrocarbon and polymer contaminants to lower the surface energy. Conversely, if our substrate were pure Teflon, one of the lowest energy solid surfaces available, we would expect most any contaminant to raise the surface energy.

We must understand what type of material (surface energy-wise) our substrate is and roughly what we expect as a contaminant. Some knowledge of the chemistries involved is therefore necessary at this point.

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If the surface energy is different, how does the contact angle change?

The Girifalco-Good-Fowkes-Young theory gives us an easy-to-use relationship between surface energy of the solid, surface tension of the test liquid, and the contact angle of the liquid on the surface. These issues are discussed in the classic reference by Arthur Adamson, *Physical Chemistry of Surfaces*, ISBN 0-471-61019-4. The following table shows representative surface energies and contact angles for water (water has a surface tension of 72.8mN/m).

SUBSTRATE	SURFACE ENERGY (mN/m)	CONTACT ANGLE (°)
Clean glass	73	0
Ordinary glass	70	20
Platinum	62	40
Anodized aluminum	50	60
PMMA	41	74
Nylon	38	79
Polyethylene	33	96
Polypropylene	26	108
Paraffin	19	110
Teflon	18	112

Basically, for ordinary surfaces exposed to air (not fabricated and maintained always in a vacuum system), surface energy will vary from 73 down to 18. Notice contact angle goes up as surface energy goes down.

What sensitivity do contact angles have for monolayer coverage?

Contact angles are determined by the upper two or three monolayers of molecules, so what is beneath this thin layer is hidden from the contact angle measurement. However, this thin layer, only 5 to 10Å thick, is what determines adhesion, electrical properties, etc., so this is exactly the depth of surface we need to measure. Contact angles will normally detect a fraction of a mono-layer of coverage, but the exact amount depends on the difference in energy between the substrate and the contaminant layer. Various studies have used XPS to correlate contact angle with monolayer coverage for specific materials, and are reported in the scientific literature.

Contact angle measurements can reliably be made industrially with ±2° accuracy (±1° with care), so the difference in angles for the two substances can be scaled into 2 monolayers using 2 or 1° measurement resolution and the difference in contact angles for the two substances.

What is the spatial resolution of a contact angle measurement?

The drops used for contact angle measurements will vary from 1mm to 5mm in diameter, so what you are measuring is the average coverage over this area. Special techniques can produce drops suitable for areas as small as 100μm square. In the other direction, large areas require a sampling technique of drops placed in a grid over the area to be checked. Most industrial contact angle measurements are done on a sampling basis, with the results averaged over 3 to 10 drops.

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