Technical Note

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Drop Shape Analyzer – DSA25

Dosing falling drops with a defined volume for contact and roll-off angles

Exact repeatability thanks to software-based generation of drops

When it comes to measurements involving falling drops, the drop size and fall height have to be kept constant if comparable results are to be achieved. If the same needle diameter is used, falling drops of the same liquid are indeed always the same size. However, it is almost impossible to specify the volume or to dose different liquids with the same volume. In this Technical Note, we will present a method which can be used to generate drops with an exactly defined volume and purposefully detach them from the needle.

Background information

Although the falling drop measurement is not a standard method for the contact angle, there are some cases where using it makes sense. For highly absorbent materials, for example, the contact angle can often only be measured – in most cases with the help of a high-speed camera – by a drop falling onto the sample. Falling drops can also be used to simulate wetting in the rain. Letting drops fall onto a sloping surface is therefore a common way of measuring the roll-off angle when analyzing self-cleaning surfaces, for example.

It is important to work with defined test parameters when dealing with such issues. Setting the fall height isn't a technical challenge. Measurement with a defined volume causes greater difficulties. If dosing is carried out until the drop falls, then the volume is only constant if both the liquid and the needle diameter are the same. Apparently, the volume can be specifically adjusted only by making tiny changes to the needle diameter, so the time and effort involved is relatively large. Not only does this circumstance make it more difficult to vary the test parameters – for instance, when adding surfactants which reduce the surface tension – but it also reduces the repeatability of wetting tests involving falling drops.

Method for dosing falling drops with a defined volume

In our *Applications & Science Center*, we have developed a method to generate drops with an exactly defined

volume and to make them fall onto the sample from the desired height.

In doing so, we use a Drop Shape Analyzer – DSA25 with a software-controlled dosing system together with our ADVANCE software. By determining the magnification, which is easy to do, ADVANCE can calculate the volume of a drop from its video image. A new feature of the software also allows users to specify the volume of the drop generated on the dosing needle. Using a control loop, the piston position of the automatic syringe is corrected until the volume's actual value is identical to the target value.

In a second step, we use the spring mechanism of one of our dosing units, which was actually developed to deposit drops in a convenient and reproducible manner. Instead of pressing the drop-depositing dosing unit downwards against the spring force as is usually the case, we lock the dosing carriage in the bottom position and then generate the drop above the sample. Once the desired volume is dosed, we release the lock and let the carrier spring upwards (see Fig. 1).

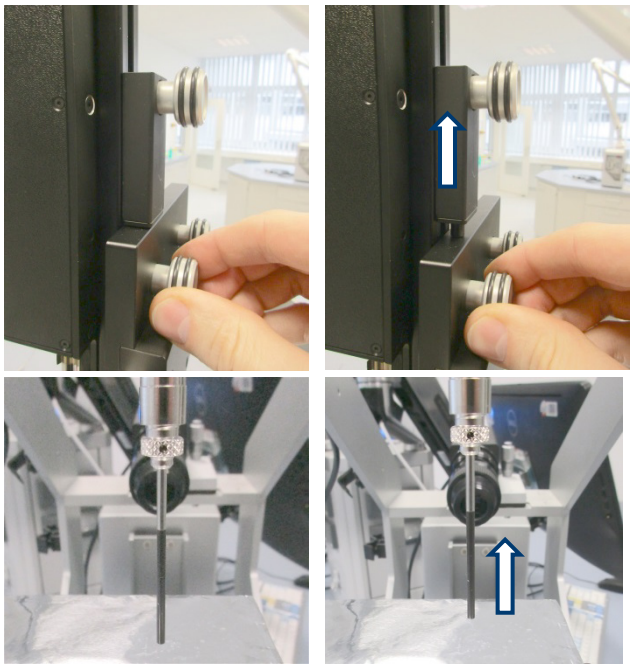

Fig. 1, top: Releasing the lock for the dosing holder's spring mechanism, bottom: Moving the needle upwards

The drop on the needle is detached and falls onto the sample (see Fig. 2).

Checking the volume accuracy

To check whether the method is suitable for falling drop analyses, it was necessary to clarify whether the dosing volume matched the volume which landed on the sample, or whether liquid remained on the needle, or satellite drops formed. To this end, the volumes were visually determined using the video image. In ADVANCE, the volume determination feature is normally used as an intermediate result when measuring the surface tension of a pendant drop (PD). Because high-accuracy literature values can be recorded for the surface tension with this method, it was safe to assume that volume is measured reliably.

First of all, we determined the volume of the PD on the needle by means of an image analysis, so as to determine the variation between the actual and the target volume achieved due to the control cycle. We then let the drop fall down from a height of 2 cm in the manner described. We determined the volume of the drop on the sample using the sessile drop (SD) method.

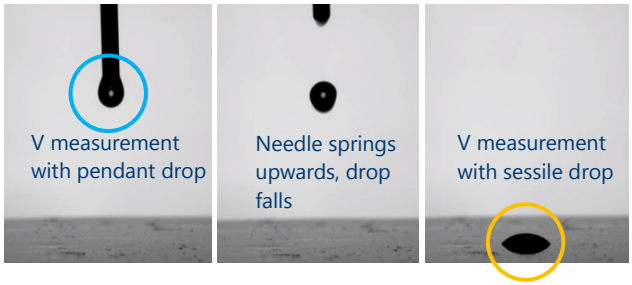

Fig. 2: Test sequence during the volume check

We used a smooth and chemically homogeneous PDMS surface as a sample for the volume test, so as to generate a symmetrical drop which could be analyzed as well as possible. Drops of the test liquids water and diiodomethane were examined with different volumes. Water is the most important liquid for many issues relating to wetting analysis, and also for measuring the roll-off angle. We also examined the dosing of diiodomethane, because this liquid is often used to determine the surface free energy of solids.

We used needles with different diameters for the various drop volumes. Thicker needles were used for larger drops to prevent premature detachment. The following standard needles from KRÜSS were used:

Needle	*Diameter*	*Material*
NE30	0.2 mm	Stainless steel PTFE-coated
NE44	0.5 mm	Stainless steel
NE62	1.0 mm	Stainless steel
NE45	1.8 mm	Stainless steel
NE33	2.0 mm	Stainless steel PTFE-coated

At least ten drops were generated and analyzed for each dosing volume during the examination.

Results of the Examination

Water

The results for water correlated very well with one another, between the target and actual volumes during the drop generation process as well as between the pendant drop (PD, blue) and sessile drop (SD, yellow) volumes as shown in Fig. 3.

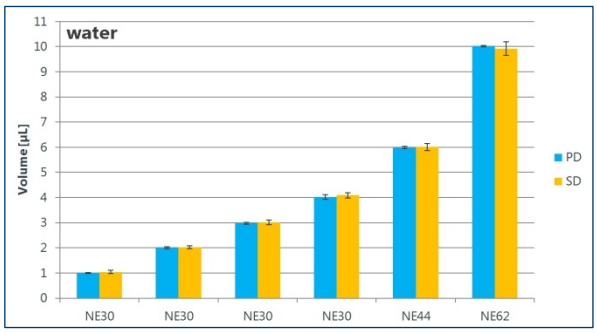

Fig. 3: Volume examination of the same drop of water, respectively, one time as a pendant drop (PD) and time as sessile drop (SD) after the drop has fallen. Mean values for at least 10 drops are shown.

The dosed liquid therefore reaches the sample entirely. The absolute difference between the actual value and the target value, and the spread of the volume measurement, tend to increase slightly as the volume increases. On the one hand, this could be related to the fact that, with the NE44 and NE62 steel needles, there was greater adhesion to the water than there was between water and the PTFE coating of the NE30 needle. On the other hand, the spread of the volume measurement for the sessile drop may only become greater as the volume increases because the drop's base surface after it hits the sample surface is no longer exactly circular – which is a prerequisite for precise volume calculation. But this circumstance only has an impact on the verifiability of the volume accuracy for large drops, not on the actual measurement of a contact or roll-off angle.

Diiodomethane

Diiodomethane has a much higher density than water (3.3 g/mL), yet has a far lower surface tension at the same time (50.8 mN/m compared to 72.8 mN/m). Both of these lead to dosed drops falling from the needle far earlier, which is why dosing has to take place with larger needle diameters (up to 2 mm in this examination).

In the case of small dosing volumes, the pendant and sessile drops still correlate well, so the method presented can be safely used for measurements involving falling drops. The dosing accuracy only becomes inadequate above 3 µL – which is quite a large volume for contact angle measurements.

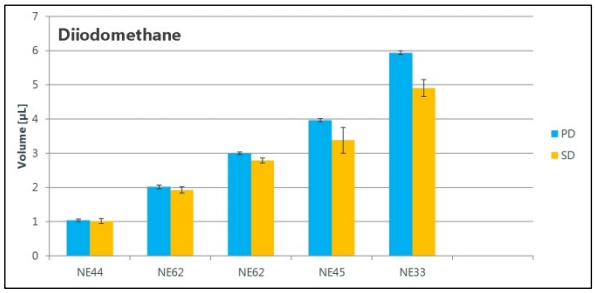

Fig. 4: Volume examination of the same drop of diiodo-methane, respectively, one time as a pendant drop (PD) and time as sessile drop (SD) after the drop has fallen. Mean values for at least 10 drops are shown.

The differences can be clearly attributed to a residual amount of diiodomethane remaining on the needle. The adhesion of a certain amount of liquid to the needle left a small pendant drop there. Volume determination of this residual drop with another PD measurement revealed that it was equal to the volume missing below. Therefore, it is possible for larger drops of diiodomethane to specify the volume of the falling drop approximately first and to determine it precisely afterwards.

Summary

This Technical Note describes a method for dosing falling drops with a predefined volume. For this, we used an automatic dosing unit and the volume measurement feature of the ADVANCE software to precisely set the dosing volume. We let the drop fall onto the sample using the spring mechanism of the dosing unit.

We checked that the volume generated correlated with the amount which landed on the sample using optical volume measurements in the context of sessile drop analyses. In the dosing liquid water, we found that the values correlated very well throughout the entire examined range of 1 µL to 10 µL. The method also worked very well for diiodomethane up to a drop size of 3 µL, and relevant deviations only resulted at higher volumes. These deviations, however, have no influence on the reproducibility of the volume of the drop when hitting the sample.

Based on the results for water and diiodomethane we are certain that the same dosing method can be used for almost any other test liquid.

On the whole, the method extends the measurement possibilities for falling drops, because there is no longer any mandatory relationship between the volume and the needle diameter and the volume can be set with a precision of 0.1 µL.

Issues for measurements involving falling drops, such as the wettability of absorbent materials or the roll-off behavior of raindrops, can thus be investigated with improved repeatability.

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