Well Prepared - Good Results

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Introduction

In recent years the demands regarding the reliability of rheological test results have grown significantly, like for most analytical methods. Only if correct test results can be produced and easily be reproduced they can be used for the reliable characterization or comparison of substances. Based on correct test results it is e.g. possible for the QC department to compare different incoming materials or different batches from production no matter whether these results have been produced on different instruments or even on different sites. It is nevertheless essential to use a viscometer or rheometer with a measuring geometry, which gives absolute results, like e.g. coaxial cylinders, plate/plate (PP)- or cone/plate (CP)-geometries. Depending on the sample's nature in can also be necessary to agree upon the test routine and data evaluation method.
Every test result contains a certain error, which is the sum of many effects mainly related to the sample, the instrument and the handling. Using the example of PP- and CP-geometries, this report will describe the preparation of a rheological test aiming to show the possible errors and how to minimize them. It is assumed that the rheometer has been installed correctly and properly levelled.

Cone or Plate? How to Choose the Right Measuring Geometry

All measuring geometries available for Thermo Scientific HAAKE rheometers have a notched top (Fig. 1). The motor axis contains a pin, which fits into the notch thus allowing the geometry to be mounted only in always the same position relative to the motor's rotor. When a calibration like the MicroStressControl (MSC) is performed to improve the data quality in the low-torque-range (nNm), its results can also be used for later test since the whole setup motor plus measuring geometry is always assembled exactly the same way.

Fig. 1: Measuring geometries with a notched cone for the well-defined mounting of the geometry (in this case rotors with ceramic shafts for high-temperature applications)

Measuring plates, used as the lower part of PP- or CP-geometries are also designed to be mounted only in one position (Fig. 2) [1].

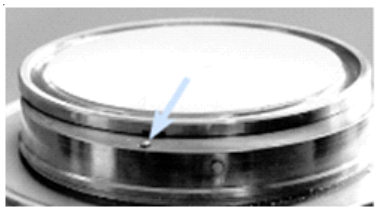


Fig. 2: Measuring plates TMP available with different diameters, the lower half of PP- and CP-geometries

In a CP-geometry, the shear rate is constant over the whole sample, whereas in a PP-geometry the shear rate decreases from its maximum value at the edge to zero at the centre of the geometry. When non-Newtonian samples are tested with a PP-geometry, viscosity values always contain an intrinsic error because different parts of the sample are exposed to different shear rates. Therefore if possible, a CP-geometry should be used for viscosity tests. Still, due to the bigger flexibility regarding the measuring gap, PP-geometries are the better and sometimes the only choice for many applications.
The diameter of the geometry has to be chosen in relation to the sample's viscosity. For water-like samples it is recommended to use cones or plates with the biggest diameter (60 mm). With increasing viscosity smaller diameters have to be used. For e.g. bitumen or hard rubber an 8 mm plate is often the best choice.
For PP- and CP-geometries the correct amount of sample becomes more important for small sample volumes and big edge effects. Therefore to load the correct amount of sample becomes more important for smaller diameters, smaller gaps and higher sample viscosities.

Determination of the Zero Gap – Reference for the Measuring Gap

Whenever a cone, a plate or the lower measuring plate has been mounted, e.g. after it had to be removed from the instrument for cleaning or when a different geometry has been chosen, the axial zero point of the geometry has to be determined. In other words, the axial position where the upper part of the measuring geometry touches the lower part is needed as the reference for precisely setting the measuring gap. Any deviation from the correct zero gap will automatically lead to an increased error of the test results due to a wrong gap size during the test.
The zero gap can be determined manually using the monitor mode in the Job Manager of the rheometer software HAAKE RheoWin (Fig. 3) or it can be implemented as an element of the test routine ("Job"), which is executed at the beginning of the test run (Fig. 4).
When using an instrument with an automatic lift (like e.g. the Thermo Scientific HAAKE MARS or RheoStress) the automatic zero gap determination cannot be forgotten and leads to a user-independent precisely determined zero gap.
To avoid any error due to thermal expansion or shrinking of the measuring geometry, the zero gap has to be determined at the temperature or start temperature of the test to be run afterwards. The upper part of the geometry can be put onto the lower

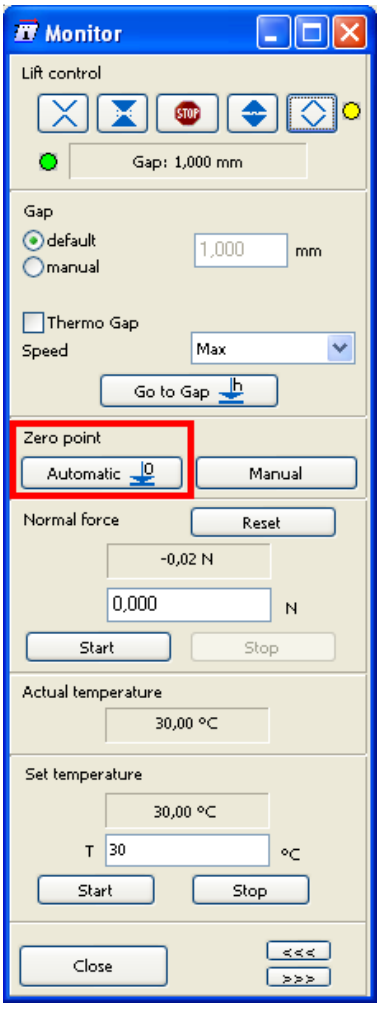


Fig. 3: Manual determination of the zero gap using the monitor mode

Sample History

The pre-treatment or history of the sample can play a crucial role for getting correct and reproducible data. The user has to design the test method keeping in mind that the sample needs to be in thermal and mechanical equilibrium before the rheological test starts i.e. by allowing a sufficiently long waiting time between closing the measuring gap and starting the test. During this time the structure of an e.g. thixotropic sample can recover from the partial destruction during the loading and closing procedure.

In some cases it is impossible to reach a stable equilibrium before starting the rheological test. Common examples are samples undergoing a chemical reaction like e.g. glues or coatings but also thixotropic samples with a very long recovery time.

When dealing with such samples, every step of the sample preparation has to be done following always the same sequence and the same timing to start all tests from the same degree of structural damage in order to get comparable data.

Newtonian fluids do not show any of the effects mentioned above. Here the focus „only“ needs to be on geometry's properties (Fig. 5) and in the appendix of the rheometer's manual.

Choosing a Suitable Measuring Gap

One of the fundamental differences between PP- and CP-geometries is linked to the measuring gap. For every cone only one correct gap exists, equal to truncation of the cone's tip. In case a different gap is needed, a cone with a different cone angle has to be used. For the typical cone angles between 0.5 ° and 4 ° the gap is usually in the range between 25 µm and 140 µm.

In contrast, the measuring gap of a PP-geometry can be varied within a certain range, so the measuring conditions can be adapted to the sample's properties.

For both PP- and CP-geometries the rule applies that the measuring gap has to be at least 3 times the diameter of the **biggest** particle in the sample to be able to measure the sample as whole and not only the particles. In the worst case some bigger particles could pile up under shear and block the gap leading to very noisy data or even damage the surface of the measuring geometry. For example, a suspension with particles up to

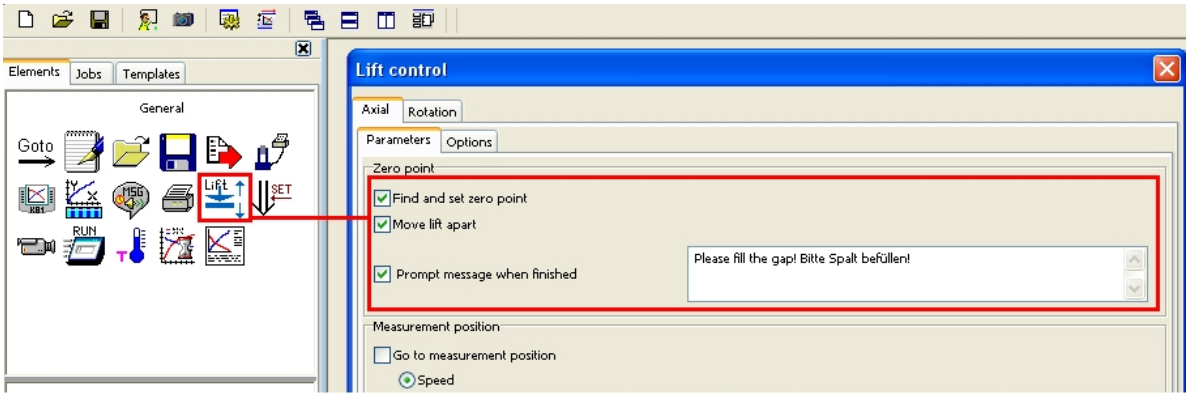


Fig. 4: Automatic determination of the zero gap using the lift control element during a test run. Here a user-defined message has been activated to ask for the sample to be filled into the geometry.

measuring plate adapted to the temperature control unit and after it has reached the desired temperature, the upper part of the geometry needs some additional time to adapt to that temperature as well. If this is done with the upper geometry already mounted, extra care has to be taken that the rheometer's air bearing is not damaged by the expanding geometry. After every part of the measuring geometry has reached the correct temperature, the zero gap can be determined and will be stored as the reference point for the measuring gap.

correct thermal equilibrium and correct gap filling, which will be looked at in more detail below.

Especially when special accessories are used like for example a sample cover with solvent trap to minimize the evaporation of the solvent in the sample or a measuring geometry with a sand-blasted or serrated surface to avoid slipping, the same set up has to be used to yield comparable results.

The sample volume needed for the correct filing of a measuring geometry can be found in the HAAKE RheoWin software as part of the

100 µm in diameter needs a gap of at least 300 µm. In this case only a PP-geometry can be used because CP-geometries with an angle bigger than 4° would not comply with the current standards and do therefore not exist.

When doing tests on foams or emulsions the measuring gap has to be chosen based on the diameter of the biggest bubbles or droplets. Otherwise the sample's properties could already be changed simply because it is squeezed into the measuring gap.

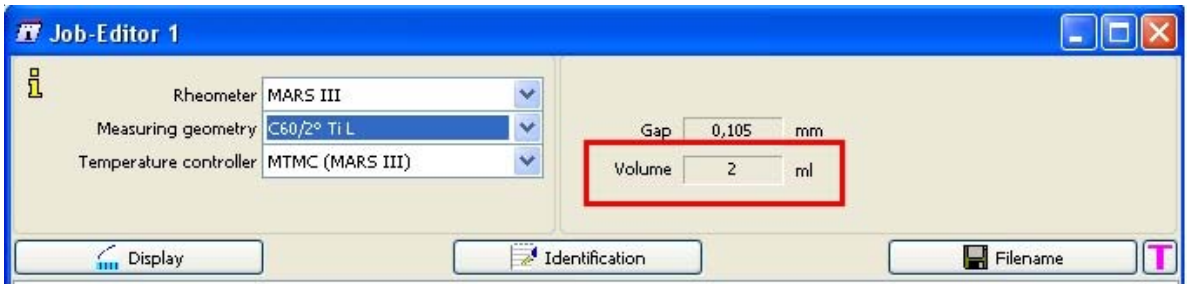


Fig. 5: HAAKE RheoWin software displaying the sample volume for correct gap filling using the example of a cone C60/2° Ti L

The upper and the lower part of every measuring geometry are produced with very high precision regarding their dimensions. After production every part is measured precisely and its diameter, cone angle and truncation are printed into an individual certificate included in the geometry's box. These parameters have to be entered once into HAAKE RheoWin and are from then on automatically available whenever the geometry is used for a test.

When a sufficiently large measuring gap is used, like e.g. 1 mm with a PP-geometry, any kind of error in parallelism can be neglected due to the tolerance of manufacturing. For very small gaps these small imperfections can lead to an error of the zero gap determination and therefore the measuring gap itself. Either a bigger uncertainty has to be taken into account for test results collected with very small gaps or even greater care has to be invested when producing and adjusting the components for such a test.

Sample Loading, Sample Trimming, Closing the Gap – the Optimum Gap Filling

Under ideal conditions, the sample fills the measuring gap completely and without any air bubbles. Around the edge of a PP- or CP-geometry the open sample surface should slightly bulge outwards.

Depending on the sample's consistency a suitable tool should be used to fill the sample into the measuring geometry. For low viscous samples a pipette can be used. For samples with a higher viscosity or stronger texture a spatula or spoon is the right tool. Samples with a delicate structure should be sheared as little as possible during the loading procedure to keep damages to the structure as small as possible. In general, the sample should be placed in the centre of the geometry.

The optimum amount of sample can be found amongst the parameters for each measuring geometry listed in RheoWin (Fig. 5). It is recommended to slightly overfill the geometry first in order to avoid remaining air in the measuring gap after closing it. Underfilling of the measuring gap has to be avoided under all circumstances!

After closing the measuring geometry the sample has to be trimmed i.e. the excess of sample that was squeezed out of the gap has to be removed with a suitable tool. Since this procedure leads to a straight sample rim, it is recommended first to go to a so-called trimming position above the measuring gap, trim the sample and then closing the geometry thus forming a slightly bulged sample rim.

As rule of thumb, a gap 1 – 5% wider than the measuring position is used as trimming position. After loading the sample this position is set either manually or automatically during a running test method in the HAAKE RheoWin software. For sensitive samples the lift speed should be reduced to minimize the damage to the sample's structure during closing the gap.

When the upper geometry approaches the trimming position using RheoWin's lift function, the axis of the rheometer is locked to avoid any damage to the sample's structure by an accidental turning of the measuring geometry. The excess sample can be removed with a lab spatula or a special trimming tool [2]. The lower plate shown in Fig. 7 has been chosen to match the upper geometry's diameter, which makes the necessary trimming procedure much easier.

For a properly trimmed sample the spatula is moved around the whole sample using the side of the lower plate as a guide (Fig. 8a). Afterwards, the rim is checked visually whether all excess has been removed. If necessary, this step has to be repeated.

Fig. 7: Lower measuring plate TMP with a diameter chosen to match the upper geometry

Especially when loading high viscous samples, it is possible that a bit of the excess sample has been pushed onto the edge of the upper geometry. During the test procedure this material could flow down again, leading to disturbing edge effects thus having a bad influence on the data quality. Therefore is it recommended, especially for high viscous samples and geometries with

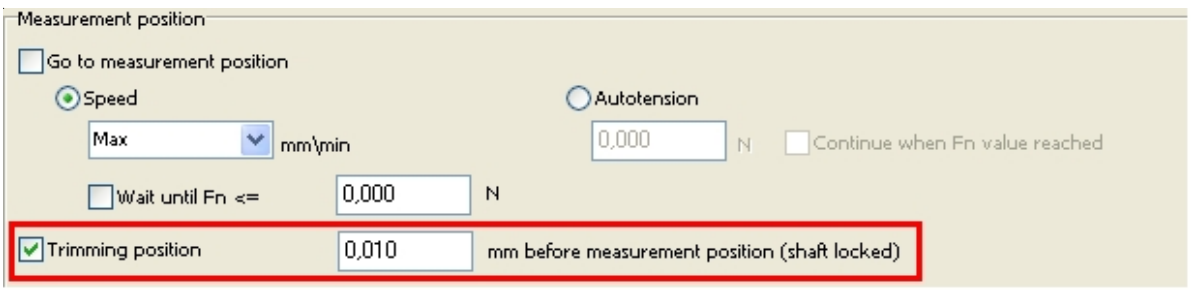
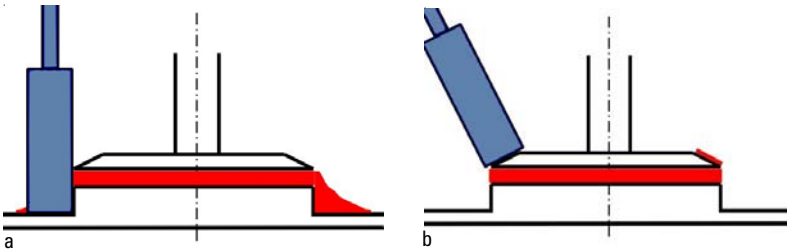


Fig. 6: The trimming position can be set in HAAKE RheoWin. Recommended are 1 - 5 % above the measuring gap chosen for the test (in the example above 10 µm and 1 mm measuring gap).



a b

Fig. 8 a: Removing excess sample with a spatula in trimming position; b: Removing excess sample from the edge of the upper geometry

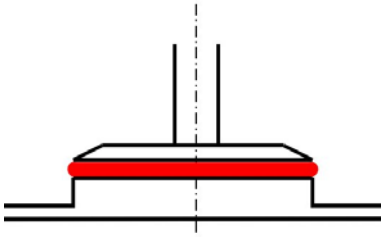


Fig. 9: Correct gap filling after closing the measuring geometry

small diameters, to strip the edge of the upper geometry from any remaining material (Fig. 8b).
Finally the geometry will move to the measuring position and the sample will get a slightly bulged rim as indicated in Fig. 9.
A perfect filling is the ideal basis for generating good data with a rheological test. As an example such a test has been described in detail in [3] using the example of a calibration oil testing.

Summary

For the determination of reliable rheological data the sample and the rheometer have to be prepared and handled carefully. Apart from selecting the right measuring geometry and determining the correct zero point, there are some steps not directly linked to the rheometer, which are crucial for the data quality. The procedure how to prepare the sample into the rheometer and how carefully the sample is trimmed afterwards are at least equally important.

Special care is needed when using small measuring geometries, small measuring gaps and high viscosities, since in these cases edge effects have a bigger influence on the data quality. In case of small measuring gaps an individual adjustment of all components involved can improve the data quality.
Following the recommendations listed in this report, the accuracy and reproducibility of rheological results can be improved significantly. Especially when rheological results have to be compared with results from other departments or other companies, accurate results are an absolute must.

References

[1] Thermo Fisher Scientific product information P029e "Exchangeable lower plates for temperature module", Cornelia Küchenmeister, Jint Nijman

[2] Thermo Fisher Scientific product information P003e "Trimming tool to remove overfilling in a plate/plate- and cone/plate-measuring geometry", Cornelia Küchenmeister, Klaus Oldörp

[3] Thermo Fisher Scientific application report V217e "Calibration fluids", Klaus Oldörp

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