Application Note
V-218

Test liquids

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Testing rotational rheometers and viscometers with test liquids

Accuracy and reproducibility of test results are of utmost importance for high-performance instruments, such as rheometers and viscometers, since they deliver basic data for both innovative product development and reliable quality control. Inaccurate or even false data can lead to substantial costs or bad investment.

Manufacturers of rheometers or viscometers[1] confirm the accuracy of the measuring instruments in writing during initial operation or after maintenance of the instruments. But, does this accuracy thereafter remain unchanged? Although the manufacturers make substantial investment in the technical progress in order to guarantee the measuring precision of their rheometers in daily use, however, in addition to that every user should regularly verify the correctness and reproducibility of his results. This is an essential component of the procedures determined in the quality handbook in many companies. The data determined is validated via regular verification. At the same time, possible discrepancy is discovered in the early stages already, so that unnecessary costs e.g. caused by a deviation from the originally desired product quality are avoided or minimized. Checking raw data i.e. torque and rotational velocity is the most accurate method of testing a rheometer. Service personnel of the manufacturer use calibrated measuring instruments with which they can directly determine torque and rotational velocity. These complex and expensive accessories are generally not available to every user.

Test liquid

For the user of a rheometer a practical and inexpensive approach to check its precision is to measure a Newtonian fluid with defined viscosity, a socalled test liquid. These test liquids have to be fully traceable to national standards and are e.g. available from Thermo Fischer Scientific - the maker of the HAAKE rheometers. They are mineral or synthetic oils whose viscosity was determined with high accuracy at one or several temperatures. The viscosity, its accuracy, the measurement temperature (normally 20°C or 25°C) and the expiry date of the test liquid are marked on the attached certificate. It is recommended to use test liquids with a viscosity similar to the one of the samples usually measured.
Impurities lead to premature ageing of the test liquids, which generally becomes obvious via a slight increase in viscosity. For this reason, any test liquid used once may not be returned into the original container.
Moreover, they should be kept in a cool, dark place. However, ageing of test liquids cannot be entirely prevented. Despite proper storage, experience shows that the viscosity increases by 1 % after 8 months. Taking into account the time between measuring the oils viscosity and delivery, the customer can rely on the certified values for at least 6 months. For testing viscotesters, silicon oils are also used since they exhibit a lower temperature dependence of their viscosity and many viscosity testers are not provided with temperature control. When using silicone oils it has to be taken into account that silicones with higher molecular weights exhibit a shearthinning effect at higher shear rates; i.e. the viscosity decreases from a specific shear rate on. Moreover, there are areas of application, such as foods, pharmaceutical products or paints, in which silicone oils may not be used at all.
Depending on the result of the test-oil measurement, one decides whether the initially measured viscosity values are correct and whether the measuring method or the rheometer must be checked. That is the reason why the measuring process must be carried out with the greatest possible care.
The following text describes, step-by-step, what must be observed in detail.

Temperature

The temperature is one of the essential influencing variables on measured viscosity. Prior to a viscosity measurement, it must therefore be ensured that the temperature in the measured gap is correct. The measuring geometry is filled with the test liquid and brought into the measuring position. The actual temperature inside the gap is measured with a suitably calibrated temperature sensor, e.g. a gap thermometer as soon as the temperature indicator remains constant. This measurement occurs separately from the viscosity measurement because a temperature sensor inside the measurement gap would disturb the correct measurement of the viscosity.

[1] For better readability, only rheometers are discussed in the following passage; the text, however, always refers to both rheometers and viscometers.

The measurement and evaluation software HAAKE RheoWin made by Thermo Fisher Scientific, for instance, provides the possibility of recording the difference between the temperature measured in the measuring gap and the indicated temperature in a so-called deviation table (Fig. 1). According to this calibration the temperature indicated in HAAKE RheoWin corresponds to the actual temperature of the sample in the measuring gap.

Measuring geometry

For the viscosity measurement the geometry is selected, which allows the widest range of shear rate for the viscosity of the test liquid. As the example in Fig. 2 shows, the test oil E200, with a viscosity of 120 mPa·s at 20°C, for instance, can be measured with a powerful rheometer, such as the Thermo Scientific HAAKE MARS, and a

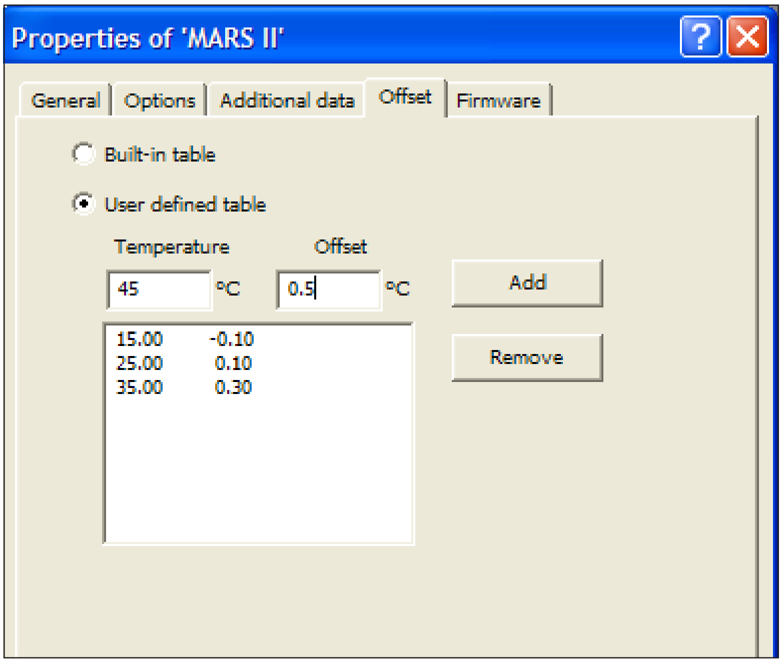

Fig. 1: Input of temperature deviations in HAAKE RheoWin

shear rates. Even though no strict standards exist for running a performance check with a test liquid, increasing the shear rate stepwise over a broader range is the recommended method.

By measuring the viscosity over a broader range of shear rate, one checks whether the instrument used measures constantly and accurately at different shear rates. After applying a constant shear stress or shear rate, it always takes a certain period of time before a constant viscosity can be measured. The application of a stepwise increasing shear rate using suitable parameters (see example in Fig. 3) enables the measurement of this constant and comparable value, the socalled equilibrium viscosity.

cone with 60 mm diameter over 5 decades in shear rate. With a 20 mm diameter cone, only 3.5 decades are possible. On the other hand, if the measuring geometry cannot be chosen freely, a test liquid with a suitable viscosity must be used.

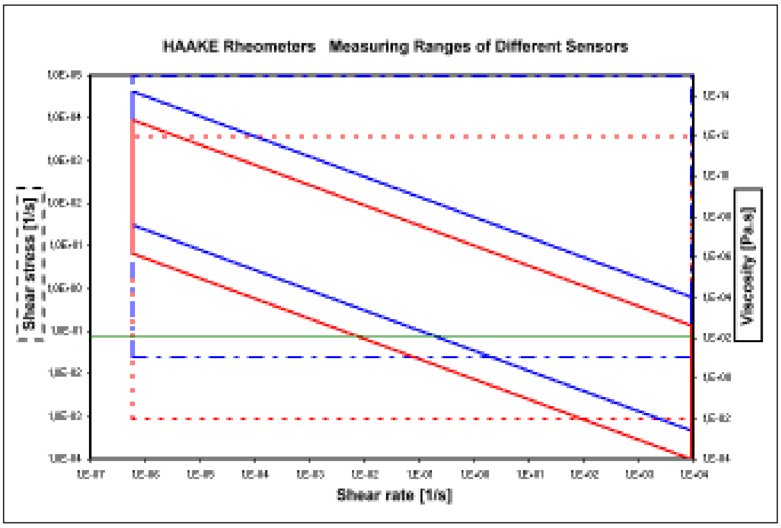

Fig. 2: Measuring range of HAAKE MARS with a cone 60 mm / 1 ° (red parallelogram) and with a cone 20 mm /1 ° (blue parallelogram). The green line corresponds to the viscosity of E200 test oil, i.e. 120 mPa·s. mPa·s.

Temperature control

After the correct temperature has been set, the selected measuring geometry is mounted into the rheometer. After the both parts of the geometry, e.g. bottom plate and cone, have adopted the measuring temperature, the zero point is determined. Now the geometry is opened again and the right amount of test liquid is added in the middle of the bottom plate. A scalable pipette can help with this. In case an exact filling is not achievable, it is better to slightly overfill than underfill the gap. The temperature of the test liquid in the measuring geometry must, if possible, exactly correspond to the temperature specified in the test liquids certificate. Apart from the calibration of the temperature display described above, it must be ensured that the temperature of the test liquid in the measuring gap is correct and constant. If, for instance, the test liquid has been directly taken from the refrigerator, it can take several minutes before the temperature is fully under control.

The time required for temperature control can be determined by means of a simple time curve. The viscosity of the test liquid is measured for e.g. 15 min under a constant shear rate or shear stress. Finally, the time after which the viscosity remains constant is determined from the measuring curve. This time plus e.g. 1 min to be on the safe side can then be used as an equilibration time for this and comparable test liquids.

Viscosity measurement

After the measuring gap has been filled correctly and the test liquid's temperature has been controlled, the actual measuring of the viscosity can take place. Viscosities can be determined for an individual shear rate or over a broader range of

The viscosity curve is evaluated with a suitable model (Newton) (Fig. 4) and the result compared with the viscosity value on the certificate. Based on experience, the device works flawlessly if the measured viscosity value lies in the range of ±5 % around the nominal value.
Since this involves real viscosity measurement, all parameters that play a role in measurements of "real samples" also influence the quality of the measured results here.
Besides the rheometer, temperature control and measuring geometry, also the location of the rheometer, the preparation of the sample and the filling level of the measuring gap can have an influence on the

results. When evaluating the measured results, these additional influences must be taken into account and corrected if necessary.

Regular checking of a rheometer by taking measurements of test liquids is always recommended. The frequency should be selected according to the sample throughput and the in-house quality standard of the company. By doing this, high-quality measured results can be guaranteed constantly and unnecessary costs and bad investment can be avoided at an early stage.

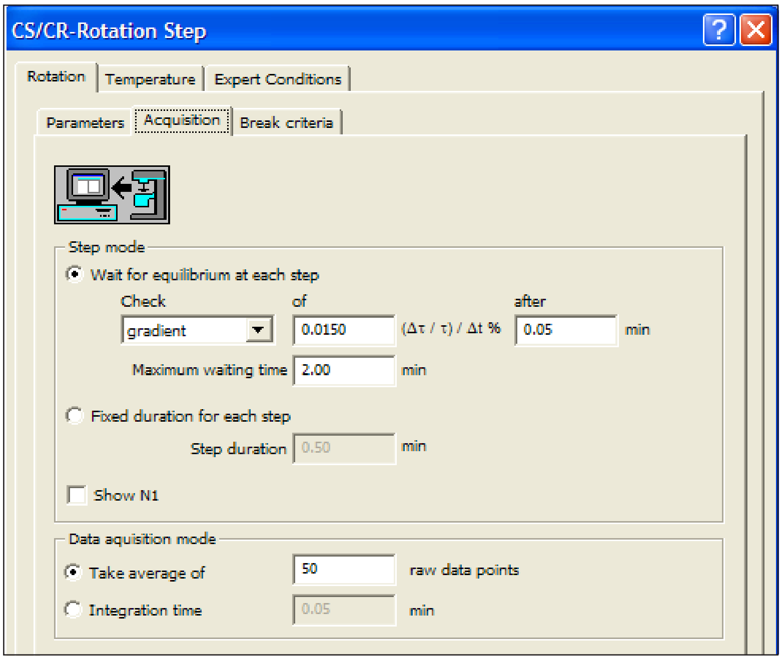

Fig. 3: Example parameter in HAAKE RheoWin, for automatically determining the equilibrium viscosity

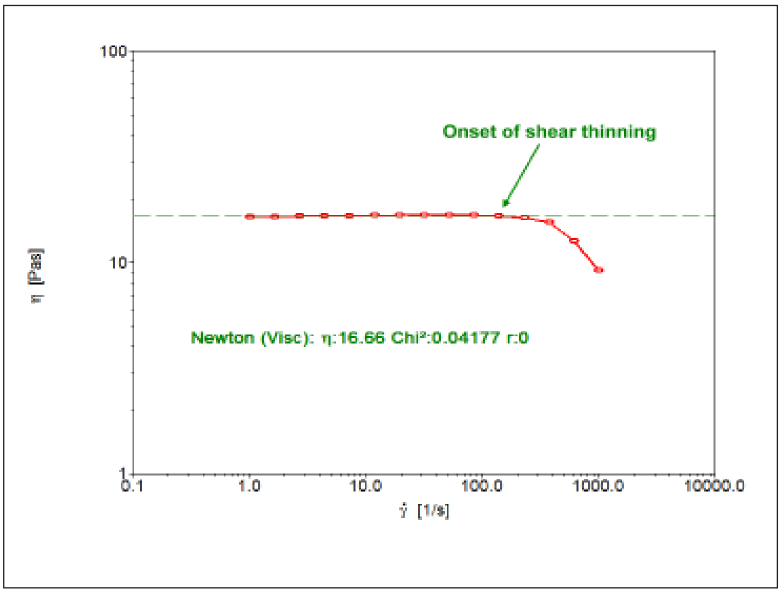

Fig. 4: Evaluation of test oil measurement with HAAKE RheoWin. The silicone oil being used shows shear thinning above 100 s^{-1}; i.e. the viscosity decreases with the increase in shear rate. Data evaluation uses only the data up to 100 s^{-1}.

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