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Advances in Viscometry

Moving beyond D445 with **D7042**

Speaker

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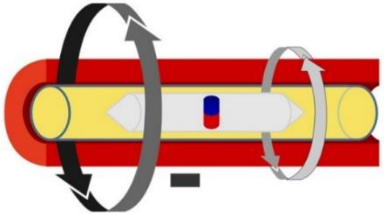
Preface

- Viscosity is a crucial indicator for petroleum and petrochemical products
- In terms of test methods, there are 2 main players:
  - ASTM D445: glass capillary viscometer
  - ASTM D7042: Stabinger viscometer (SVM)
- In this presentation, we objectively reference data from the ASTM to explain
  - the D7042 test method
  - the differences between D7042 and D445
  - that D7042 precision and accuracy matches D445
- Comparisons are made based on data from ASTM D7042-21a and ASTM D445-23

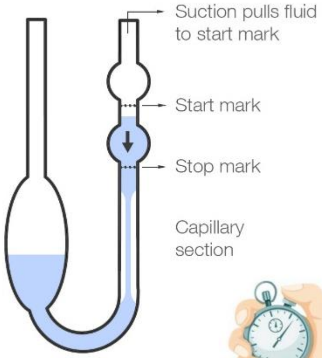
A Quick Comparison

D7042



- SVM test method
- Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)
- Introduced in 2004

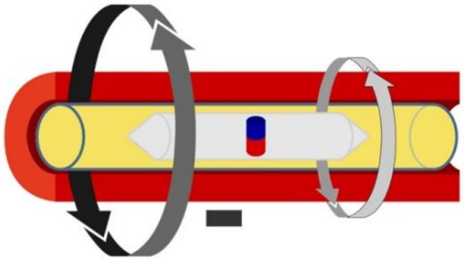
D445



- Capillary test method
- Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity) by glass capillary viscometer
- Introduced in 1937

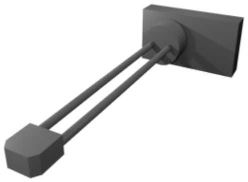
Principle of D7042

- Sample is filled into the measuring cell
- Dynamic viscosity is measured by a coaxial cylinder measuring system
- Density is measured by oscillating U-tube
- Kinematic viscosity is automatically calculated
  - $\nu = \frac{\eta}{\rho}$
    - η…dyn. vis
    - ρ… density
- High precision (r ~ 0.09 %; R ~ 0.58 %)
- Also known as ISO 23581



coaxial cylinder measuring system

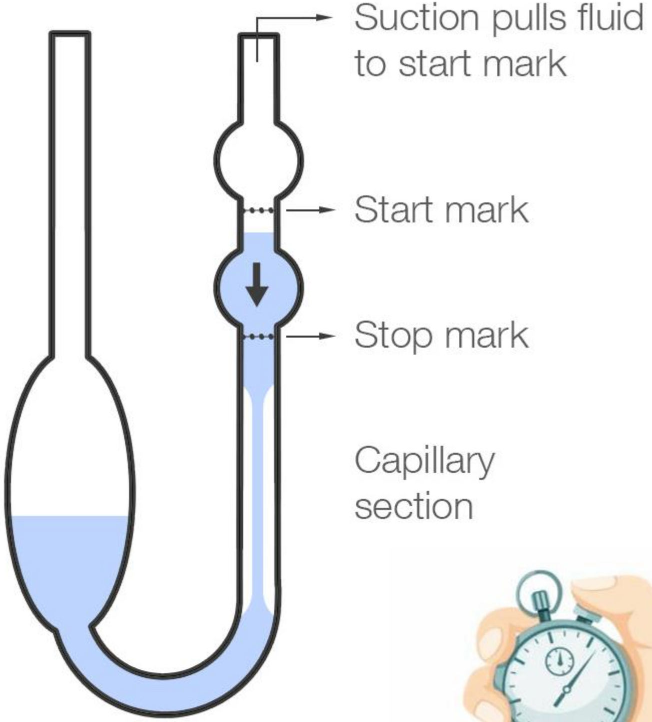
+



Oscillating U-tube

Principle of D445

- Sample flows through a calibrated capillary under gravity at a controlled & known temperature
- Flow time is measured
- Kinematic viscosity is manually calculated
  - $\nu = C * t$
  - t… flow time
  - C… viscometer constant
- Usually good precision (r ~ 0.5 %; R ~ 1%)
- Also known as ISO 3104 or IP71/1



D445 in Detail

D445 main components

- Temperature Control / Heating element
- Liquid Bath
- Thermometer
- Glass capillary (viscometer)

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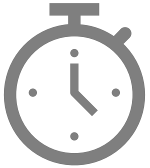


Stopwatch

D445: from cheap to expensive

- There are manual systems, semi-automatic, and automatic systems
- All of them come in many different configurations: bath geometry, temperature range, number of capillaries that can be mounted at once

manual → automatic

cheap → expensive

Adjustment D445

- Use only calibrated viscometers […] => D446
- If the determined kinematic viscosity does not agree […] re-check each step […] to locate the source of error.
- The most common sources of error are caused by particles of dust lodged in the capillary bore and temperature measurement errors.
- The calibration constant, C, depends on the place of calibration. This is to be supplied by the standardization laboratory together with the instrument constant.

Adjustment D446/D2162

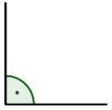
- Select a calibrated viscometer of known viscometer constant *C*1. 2 oils, 50 % flow time difference, max. 0.2-0.3 % deviation […] See Test Method D2162.
- D2162:
  - “step-up” from the kinematic viscosity of the primary standard to the kinematic viscosities of oil standards due to surface tension or differences in kin. vis.
  - Calibration of at least 2 master viscometers having calibration constants in the 0.001 mm^2/s^2 to 0.003 mm^2/s^2 with water at 20 °C
  - Then two or more oil standards are measured at 40 °C
  - Corrections are made for buoyancy and, where necessary, for temperature and surface tension
  - A third master visc. (calibration constant from 0.003 mm^2/s^2 to 0.009 mm^2/s^2) undergoes calibration at 40 °C using the two standard oils and the calibration factor determined at standard conditions for water at 20 °C
  - Additional viscosity oil standards and additional master viscometers: calibrated at 40 °C using the average results from at least two master viscometers or two oil standards
  - Steps between calibration constants or viscosities by factor of 3 or less until desired range is covered
  - Other temperatures: average results from at least 2 master viscometers

D445 compliant measurement

100% complying to D445 with a glass capillary is difficult!

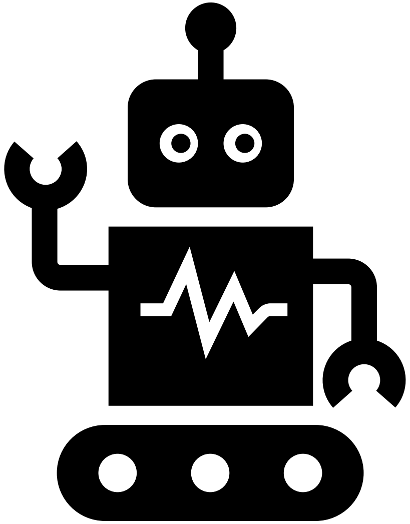
- “[…] the **temperature control** of the bath liquid shall be such that […] the temperature of the bath medium does not vary by more than ±0.02 °C of the selected temperature over the length of the viscometer […]”
- “[…] [temperature] **probe** shall be recalibrated when the check value differs by more than 0.02 °C from the last probe calibration […]”
- “Regularly check **timers** for accuracy […]”
- “Use viscometer **holders** to enable all viscometers which have the upper meniscus directly above the lower meniscus to be suspended vertically within 1° in all directions. Those viscometers whose upper meniscus is offset from directly above the lower meniscus shall be suspended vertically within 0.3° in all directions.”
- “establish a safe **equilibrium time** by trial” – “minimum of **30 min** is specifically required for manual analysis of jet fuels at −20 °C”
- “The **flow time** for manual viscometers shall not be less than **200 s** […]”





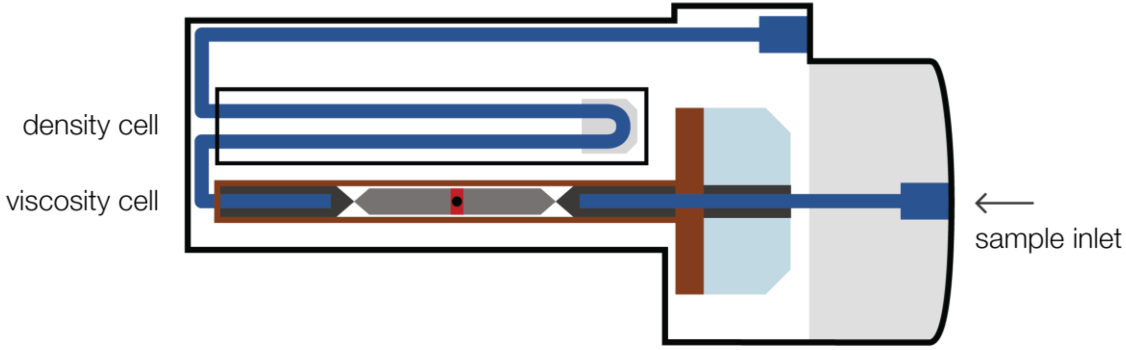

Automated D445 Systems

- Apparatus, which has mechanized one or more of the procedural steps without changing the principle or technique of the basic manual apparatus (mimics some operation of the test method)
- Flow times of <200 s permitted
  - Kinetic energy correction shall be applied
- Determinability, repeatability, and reproducibility is no worse than manual apparatus for distillates, FAME at 40 °C, base oils at 40/100 °C, formulated oils at 40/100°C
- No bias to manual data
- Same limitations as manual (only kin. Vis., small viscosity range, one bath per temperature due to long equilibration times)



D7042 in Detail

Principle of D7042



SVM™ Measuring Cells

- Dynamic viscosity is measured using a coaxial cylinder measuring system
- Density is measured by Oscillating U-tube method in accordance with D4052
- Kinematic viscosity is calculated by dividing the dynamic viscosity (η) by the density (ρ):

$$\nu = \frac{\eta}{\rho}$$

D7042 conform measurement

1. Fill the measuring cell with ≥2 mL sample avoiding the introduction of air bubbles and start the motor.
2. After 10 s fill an additional ≥1 mL sample and start the measurement:
   1. The viscometer will measure the rotational speed of the inner cylinder and calculate the viscosity based on the difference to the outer cylinder that is rotating at a constant speed.
   2. Allow the measurement to stabilize without interruption.
3. Once the measurement is complete, inject another ≥1 mL of sample and repeat the measurement
4. If the deviation between two consecutive lies within the determinability limits* the determination is valid.

-> You now have a D7042-conform result (approx. 6 min per sample)

*detailed for different sample types in D7042 – Table 1

D7042 conform measurement

- Before the measurement (Preparation):
  1. Sample Preparation: Ensure the sample is well-mixed and free of bubbles and particulates.
  2. Turn on the Viscometer
  3. Set the measurement temperature on the viscometer, ensuring it is appropriate for the sample being tested (maximum temperature range: -60 °C to +135 °C)
  4. Make sure the measuring cell is clean and dry.

- After the measurement (Cleaning):
  - After the measurement is complete, remove the sample immediately, thoroughly rinse with suitable solvent and dry the measuring cell with a pressurized air flow

D7042 key features

- Gives multiple parameters (kin. and dyn. viscosity, density, VI, etc.) from one syringe
- Wide viscosity range with one measuring cell (0.2 to 30 000 mm^2/s)
- Low sample and solvent volume (min. 2 mL)
- Wide temperature range (-60 °C to +135) without any external bath
- Extremely fast heating/cooling rates (up to 20 °C/min)
- Temperature scan possible
- Unbeatable ease of operation: fill the sample from a syringe and press start

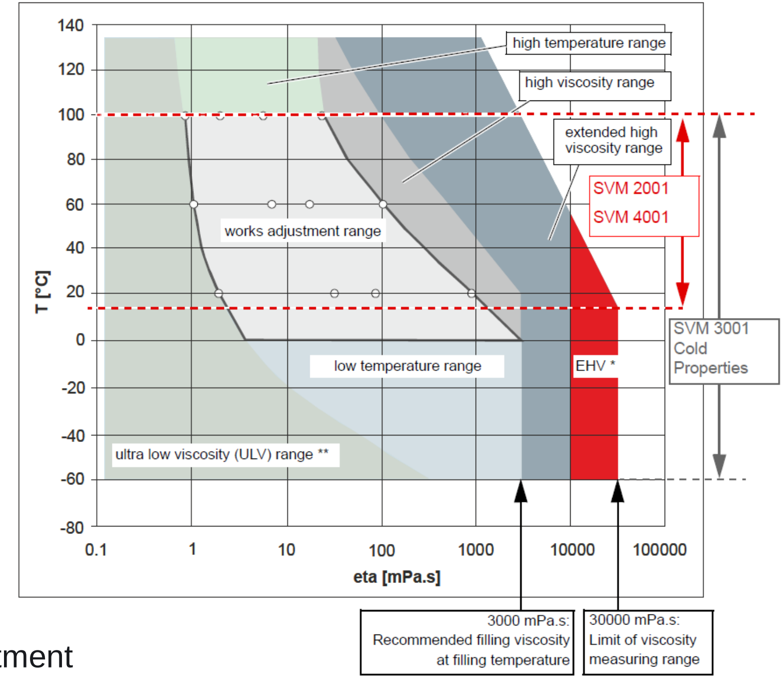
Adjustment D7042

Directly from D7042:

- 9.2 *Certified Viscosity and Density Reference Standards*— These are for use as confirmatory checks on the procedure in the laboratory. Certified viscosity and density reference standards shall be certified by a laboratory,
- 9.3 *Thermometer*—For calibration and adjustment of the temperature control, a digital thermometer with a probe […]
- 10.1 An adjustment has to be carried out when repeated calibration check measurements do not agree with the Acceptable Tolerance Band
- 10.2 For an adjustment, use only certified viscosity and density reference standards that fulfill the requirements as stated in 9.2. The reference standards have to be within the viscosity, density, and temperature range specified by the manufacturer of the apparatus.

Full Range Adjustment of a D7042 Viscometer

- Temperature
  - before ρ, η
- Density ρ
  - air density + viscosity std. (values for dyn. visc. & density from certificate)
- Viscosity η (12 Points – 4 oils, 3 temperatures)
  - Temperature vs
  - speed ratio tube:rotor ∝ viscosity
  - L (S3), M (N7.5), H (N415), C (N26); special oils for HT/LT adjustment
  - to cover a visco range from 1-1000 mm²/s
  - 20, 60, 100 °C → best ρ, η, T distribution



Bias-Corrected D445 results from D7042 measurements

Can a D7042 measurement be D445-conform?

6. Apparatus

6.1 *Stabinger Viscometer*[6,7]

6.1.1 *Viscosity Measurement*—The Stabinger viscometer uses a rotational coaxial cylinder measuring system. The outer cylinder (tube) is driven by a motor at a constant and known rotational speed. The low-density inner cylinder (rotor) is held in the axis of rotation by the centrifugal forces of the higher density sample and in its longitudinal position by the magnet and the soft iron ring. Consequently, the system works free of bearing friction as found in rotational viscometers. A permanent magnet in the inner cylinder induces eddy currents in the surrounding copper casing. The rotational speed of the inner cylinder establishes itself as the result of the equilibrium between the driving torque of the viscous forces and the retarding eddy current torque. This rotational speed is measured by an electronic system (Hall effect sensor) by counting

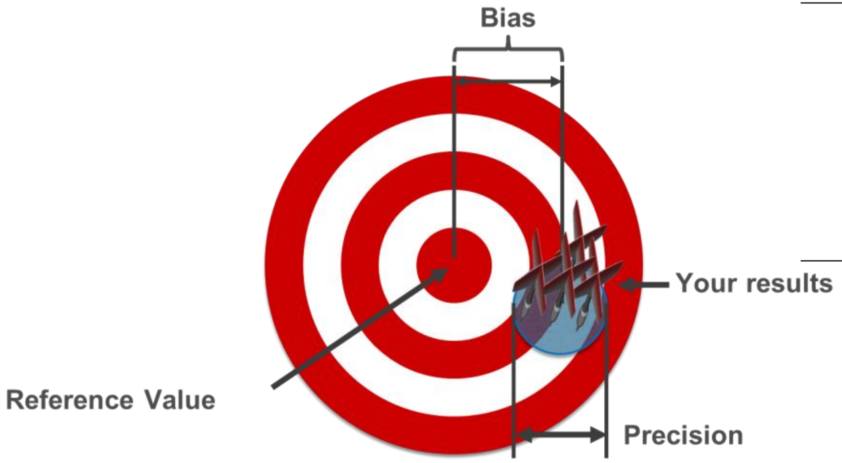
6. Apparatus

6.1 *Viscometers*—Use only calibrated viscometers of the glass capillary type, capable of being used to determine kinematic viscosity within the limits of the precision given in the precision section.

NO, but...

… with use of the implemented bias correction, it is possible to:
- measure in accordance to D7042 and
- report data that complies with D445.

The bias correction factors were determined not by the manufacturer, but by statisticians at ASTM, utilizing data from a globally conducted interlaboratory study.



How to determine Precision & Bias

By Inter-Laboratory Studies (ILS), also known as round robin organized by ASTM

1. Perform tests

Different laboratories round the globe measure samples with e.g. D7042 and D445 instruments under predefined conditions

2. Gather data

Results are documented in a Research Report (RR), which includes reproducibility (R) and repeatability (r) of both test methods

3. Derive bias statement

Formulas for bias corrections are derived by ASTM

AP is using these published data for the bias corrections in SVM

D445 bias correction

- The bias between D7042 and D445 is defined based on results from worldwide ILS
- ASTM developed formulas for different products and temperatures for bias correction between D7042 and D445
- These formulas are implemented in D7042 viscometers
- It is important to choose the right material & temperature
  - Exmaple: if your sample is biodiesel & you measure at 40°C → choose Biodiesel bias correction at 40°C

TABLE 4 Suggested Relative Bias Correction to Manual D445 Kinematic Viscosity

Material	Temperature °C	Relative Bias Correction, mm^2/s^A	Bias-corrected X (predicted Y) = mX+b mm^2/s
Base Oils	40 and 100	none	m=1, b=0
Formulated Oils	40	0.996X	m=0.996, b=0
Formulated Oils	100	X-2.3538e-02	m=1, b=-2.3538e-02
Diesel fuels	40	0.9872X-0.00015	m=0.9872, b=-0.00015
Jet fuels	–20	1X-0.013373	m=1, b=-0.013373
Biodiesels	40	0.992X+0.022	m=0.992, b=0.022
Residual fuel oils	100	1X+0.251	m=1, b=0.251
Jet fuels, scanning	–20 and –40	N/A	N/A

This means the measurement results with D7042 are practically equivalent to measurement results with D445 for these samples at the given temperatures, provided the bias correction is applied

ASTM D7042
Bias-Corrected D445 results

ASTM 7042 includes bias statements for:

- Base oils (40/100 °C)
- Formulated oils (40/100 °C)
- Diesel Fuel (40 °C)
- Biodiesel (40 °C)
- Jet Fuels (-20 °C)
- Jet Fuels, scanning (-20 °C and -40°C)
- Residual fuels oils (50/100 °C)

For Samples included in the list,
D7042 and D445 are equivalent,
if the bias correction is applied.

Example for bias correction

Example for a formulated oil at 40 °C:

- The suggested bias correction is: Y-Estimate (0.996) multiplied with “D7042 result“ (X)
- D7042 result = e.g. 9.199 mm²/s
- Bias corrected D445 result = 0.996 * 9.199 mm²/s = 9.162 mm²/s

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Formulated Oils	40	0.996X	m=0.996, b=0
Formulated Oils	100	X-2.3538e-02	m=1, b=-2.3538e-02
Diesel fuels	40	0.9872X-0.00015	m=0.9872, b=-0.00015
Jet fuels	–20	1X-0.013373	m=1, b=-0.013373
Biodiesels	40	0.992X+0.022	m=0.992, b=0.022
Residual fuel oils	100	1X+0.251	m=1, b=0.251
Jet fuels, scanning	–20 and –40	N/A	N/A

Precison of D7042

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D445 vs D7042

The Precision is on par!

Base Oils at 40 °C	D7042	D445
Instrument	SVM	Glass capillary
Repeatability r(95)	0.09 %	0.11 %
Reproducibility R(95)	0.58 %	0.65 %

Jet fuels at -20 °C	D7042	D445
Instrument	SVM	Glass capillary
Repeatability r(95)*	1.07 %	1.24 %
Reproducibility R(95)*	1.86 %	2.19 %

*@ 7.98 mm^2/s

Formulated oils at 40 °C	D7042	D445
Instrument	SVM	Glass capillary
Repeatability r(95)	0.64 %	1.07 %
Reproducibility R(95)	1.16 %	1.90 %

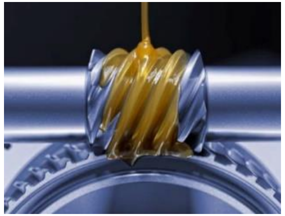
at 150.7 mm^2/s

Residual fuel oils at 50 °C	D7042	D445
Instrument	SVM	Glass capillary
Repeatability r(95)	9.1 %	7.9 %
Reproducibility R(95)	10.3 %	8.5 %

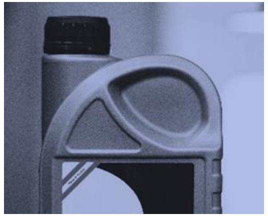
Repeatability = same lab, short intervals
Reproducibility = between labs

D7042 is referenced in numerous ASTM specifications

At a glimpse...



Lubes
ASTM D2270 (VI), SAE J300 (engine oil)



Hydraulic Oils
ASTM D6158, D8029 (mineral & bio)

Transformer Oils
ASTM D2140, D2501

Distillate Fuels
ASTM D396, D975, EN 590 (Diesel) & many more

Heavy/Residual Fuels
ASTM D396 (fuel oils)

Aviation Turbine Fuels
ASTM D1655, D7566, Def Stan 91-91, JIG AFQRJOS

In detail…

- D396 Standard Specification for Fuel Oils:

  7.1.7 *Viscosity*—Viscosity may be determined in accordance with Test Method D445, D7042, or D7945. Test Method D7945 may be used with the same limits as Test Method D445 for Grades No. 1 through No. 4 and B6-B20. Bias-corrected values from Test Method D7042 may be used as alternative results for Test Method D445 with the same limits for all grades. Section 15 of Test Method D7042 contains bias-correction information. In case of dispute, Test Method D445 shall be used as the referee method.

- D2880 Standard Specification for Gas Turbine Fuel Oils:

  6.1.7 *Viscosity*—Test Method D445. Bias-corrected values from Test Method D7042 may be used as alternative results for Test Method D445 with the same limits. Section 15, Precision and Bias, of Test Method D7042 contains bias-correction

- D1655 Standard Specification for Aviation Turbine Fuels:

Viscosity –20 °C, mm^2/s^M	max	8.0	D445/IP 71, Section 1	D7042[N] or D7945

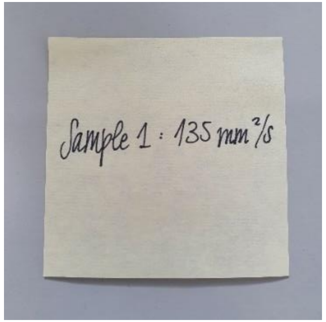
[N] Test Method D7042 results shall be converted to bias-corrected kinematic viscosity results by the application of the correction described in Test Method D7042 for jet fuel at –20 °C (currently subsection 15.4.4).

Summary

Data collection

ASTM D445

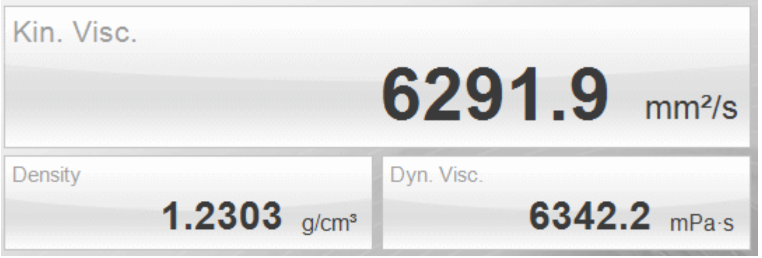
- Measures one parameters
  - Kinematic Viscosity



*Dyn. Vis. only if density is known

ASTM D7042

- Measures multiple parameters
  - Kinematic Viscosity
  - Dynamic Viscosity
  - Density



Viscosity Range

ASTM D445

- Tight viscosity range of one single capillary
- sample and solvent volume depending on used capillary 12-20 mL

ASTM D7042

- Instrument covers the whole viscostiy range
- Low sample and solvent volume
  - Min. 5 mL sample & 3 mL solvent
- Up to 85 % lower solvent consumption
- Up to 70 % lower sample needed

Thermoregulation

ASTM D445

- Liquid bath required for temperature control
- Temperature range limited by bath liquid
- Temperature changes and equilibration take long
- Only fix temperature, no temp. scan

ASTM D7042

- Thermoelectric heating and cooling system without bath
- fast heating/cooling rates (up to 20 °C/min)

Sample Handling

ASTM D445

- Check the approximate viscosity of the sample
- Chose the correct capillary
- Temperature equilibration
- Etc.

ASTM D7042

- Fill the sample from a syringe
- Fress start
- Short equilibration time due to thermoelectric heating
- No hot, flammable or toxic bath liquids required to cover the full temperature range

Results

ASTM D445

- Measurement of flowtime
- Calculation of kinematic viscosity

ASTM D7042

- Immediate output of kinematic viscosity value
- No source of error due to manual transcription and calculation
- No additional equipment required for calculation

Questions

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