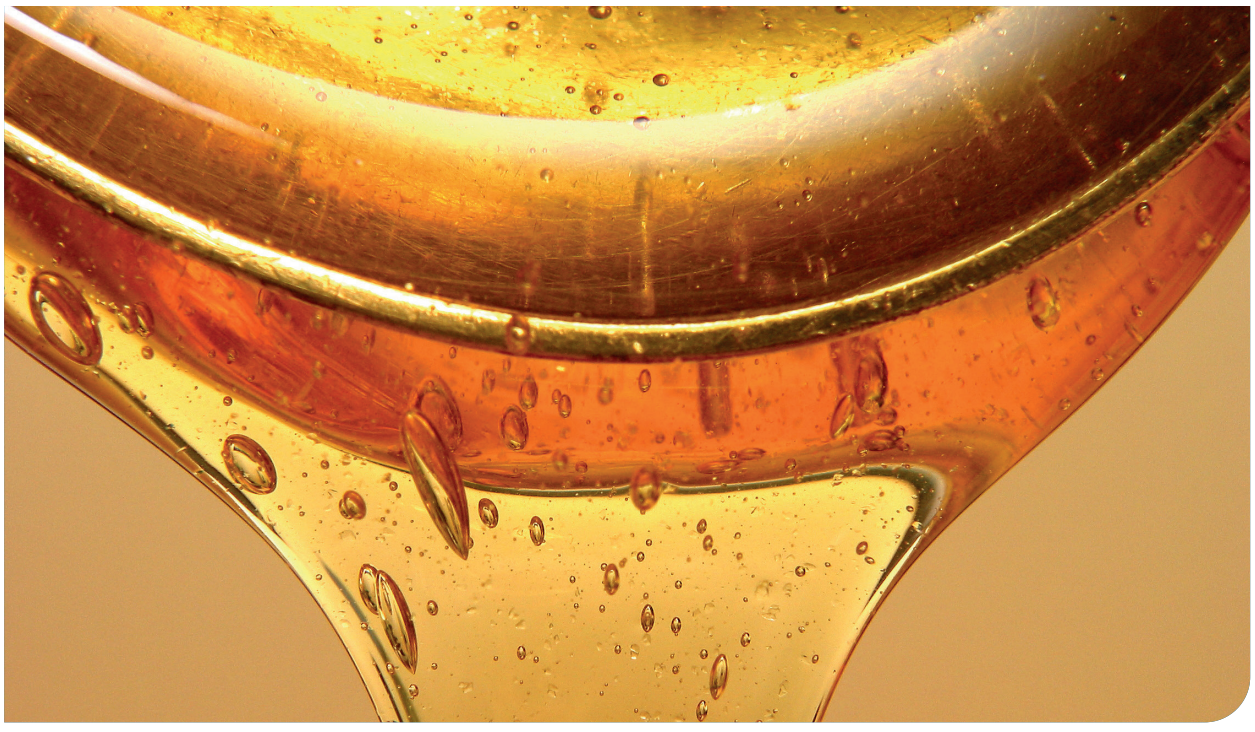
NEW TEST METHODS AND BIAS CORRECTIONS: ASTM D7042 AS A VISCOSITY MEASUREMENT ALTERNATIVE

With the petroleum industry representing a market heavily driven by standards, compliance with national and international norms is of the utmost importance. For each specified parameter, allowed test methods are reported, and discussions about the inclusion of novel alternates to established procedures have always been an important part of the standard development process. Common points to be addressed typically involve the precision of the new alternatives for the sample types and property ranges under investigation as well as the bias with regard to existing methods. Hence, standard development organizations (SDOs) have established statistical methodologies to provide conclusive data to the respective committees as a basis for decision-making. Upon positive evaluation of the newly proposed method and its incorporation into the specification, formulae derived from statistical data generated in the process may be utilized by the end user of the standard. This enables users of the alternate method to report results that can be considered practically equivalent to the reference method.



In this article, after a brief introduction to terminology, we will elaborate how statistical equations documented in alternate test methods can aid in reporting bias-corrected measurement results, using the kinematic viscosity test methods ASTM D445[1] and the novel ASTM D7042[2] as examples.

Precision, Bias, and Inter-laboratory Studies

According to ISO 5725[3], the accuracy of a test method is defined by both its trueness or bias and its precision. Trueness represents the closeness of agreement between the arithmetic mean of a large number of test results and a true or accepted reference value, while precision depicts the closeness of agreement between test results, or variability between repeated measurements due to random errors, respectively (Figure 1). Both terms constitute the accuracy, which is the closeness of agreement between a test result and the accepted reference value.

The precision of a test method evaluates the order of magnitude of random errors attributed to the measurement and is influenced by, among other things, the operator, equipment, calibration, the environment (e.g., temperature and ambient humidity), and the time between measurements. In this context, the repeatability (r) is defined as the variability of results when the influencing factors are constant, i.e., measurements with the same operator, equipment, and in the same environment within a short period of time. The reproducibility (R), on the other hand, denotes the variability of results when the influencing factors are changing, i.e., varying operator, equipment, and/or environment as well as a long time between the measurements. Consequently, r represents the smallest possible variability of the method, while R represents the largest.

The trueness or bias of a test method is related to the variability between repeated measurements due to systematic error and hence describes the difference between the population mean of test results and an accepted reference value. Such bias may exist not only between laboratories but also between measurement methods.

Both precision (r, R) and bias are determined as part of the standard development process by SDOs in inter-laboratory studies (ILSs) or "round robins." In such studies, different laboratories perform measurements on a specific set of samples under specified predefined conditions (temperature, etc.) with at least two test methods, a new procedure to be characterized, and a reference method. Subsequently, the results are evaluated and a research report (RR) is generated, which includes the precision of both methods, the bias between the methods as well as formulae, which permit bias corrections of measurement data. The findings of the research reports are then summarized in the respective test methods.

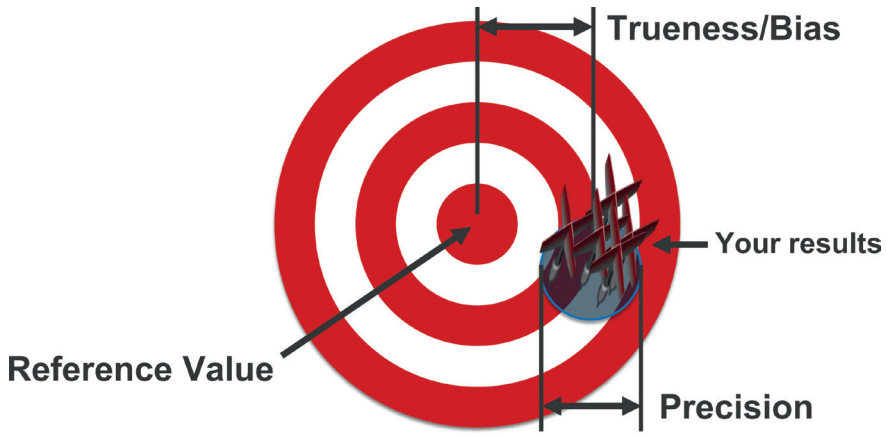


Figure 1: Precision: variability due to random errors inherent to the measurement. Bias: variability between repeated measurements due to systematic error.

Example: Measurement of Kinematic Viscosity Using ASTM D445 and ASTM D7042

Both methods, ASTM D445 and ASTM D7042, allow the indirect determination of kinematic viscosity on a variety of transparent and opaque liquids. ASTM D445 was first approved in 1965 and uses glass capillaries, typically held at a constant temperature by immersion in a temperature-controlled liquid bath. The apparatus may either be operated manually or in an automated fashion (Figure 2). Following the introduction of the test specimen into the capillary, it is pulled to the start mark by suction. The time required for the liquid to flow from the start to a stop mark (driven by gravity) is measured and the kinematic viscosity is calculated by multiplication of the measured time with a viscometer constant (C):

$$v = C * t$$

v = kinematic viscosity in mm^2/s

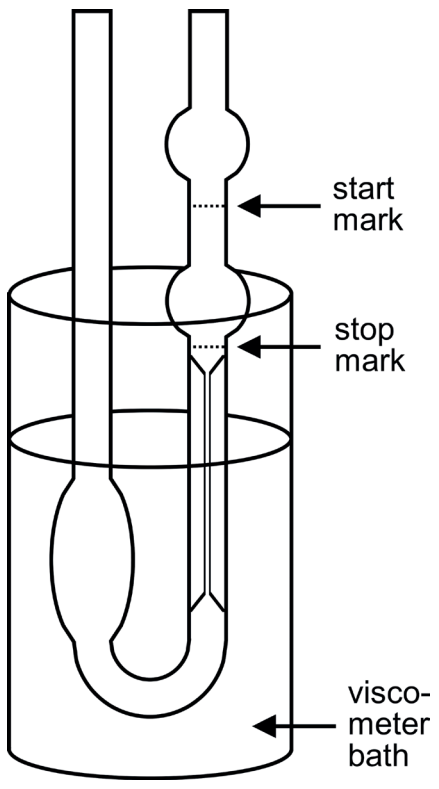
C = viscometer constant

t = time in s

Precisely following ASTM D445, however, is cumbersome because the test method – for example –has very little tolerances for the alignment of the capillary and thermometer/DCT probe in the liquid bath and requires patience when waiting for temperature equilibration.

Due to its historical origin, ASTM D445 is often regarded as the reference method for determining kinematic viscosity. However, several drawbacks, including the above-mentioned stringent operational requirements, high solvent and energy consumption, and difficult cleaning and handling due to the risk of glass breakage, have driven the development of more modern alternatives.

ASTM D7042 is a comparatively recent method, first released in 2004, and describes the Anton Paar SVM™ Smart Viscometer (Figure 3). The test specimen is introduced into the measuring cells, which are at a closely controlled and known temperature and consist of a pair of rotating concentric cylinders and an oscillating U-tube. The dynamic viscosity is determined from the equilibrium rotational speed of the inner cylinder under the influence of the shear stress of the test



specimen and an eddy current brake, while the density is obtained by the oscillation frequency of the U-tube, both in conjunction with adjustment data. The kinematic viscosity is subsequently calculated automatically by dividing the dynamic viscosity (η) by the density (ρ):

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

v = kinematic viscosity in mm^2/s

η = dynamic viscosity

ρ = density

Utilizing this instrument/the new test method (ASTM D7042) has several benefits for the user:

- Multiple parameters are determined simultaneously: dynamic viscosity, density, and kinematic viscosity.
- A broad viscosity range of 0.2 mm^2/s to 30.000 mm^2/s is accessible with one measuring cell in contrast to the very limited range of a single glass capillary (e.g. 0.5 mm^2/s to 3 mm^2/s for capillary "0C"). This is particularly valuable when samples with completely unknown viscosity need to be characterized: The tedious search for the right glass capillary becomes unnecessary.
- Lower economic and environmental impact through lower sample and solvent consumption (3 mL to 5 mL versus 12 mL to 20 mL).
- Faster temperature changes and equilibration times are facilitated by the integrated thermoelectric heating and cooling system in comparison to viscometer baths.
- The sample is filled from a syringe and cleaning and drying is done in situ, which is a much simpler process compared to glass capillaries, which need to be removed from the thermostat bath for cleaning.

In addition to the practical advantages, ASTM D7042 is also a well-accepted standard and, at the time of this writing, is referenced in more than 50 norms. These include specifications for fuel and (bio-) diesel fuel oils (ASTM D396[4], D975[5], D6751[6], D7467[7]), gas turbine fuels (ASTM D2880[8]), aviation turbine/jet fuels (ASTM D1655[9], D7566[10], JIG AFQRJOS[11], and Def Stan 91-091[12]), kerosene (ASTM D3699[13]), burner fuels (ASTM D6448[14], D7666[15]), hydraulic and engine oils (ASTM D6158[16], SAE J300[17]), and more. Finally, the viscosity index can also be calculated according to ASTM D2270[18] from kinematic viscosity data obtained using test method ASTM D7042.

Bias Corrections: Significance and Application

In spite of the benefits, the measuring apparatus of ASTM D7042 is markedly different from ASTM D445, and thus a bias between these methods has been determined by ASTM in inter-laboratory studies for many different sample types, including base oils, formulated oils, diesel fuel, biodiesel, jet fuels, and residual fuel oils at various temperatures. Many specifications, which list ASTM D7042 as an alternative to ASTM D445, require the user to apply a bias correction in order to comply.

To facilitate this, ASTM D7042 specifies bias-correction equations for data obtained by this method. Figure 4 shows a fictional example.

D7042 result * bias correction factor = Bias corrected D445 result

X * 1.004 = Y - Estimate

D7042 result: 9.199 mm^2/s

Bias corrected D445 result: 9.199 * 1.004 = 9.236 mm^2/s

Figure 4: Fictional bias-correction example.

Some of these formulae are more complex, but notably all necessary equations have already been implemented in the software of SVM™ for convenience and, therefore, no manual calculations are necessary. In addition, since bias corrections are only valid for certain temperatures, only corrections that apply to the set measuring cell temperature can be selected in order to avoid errors.

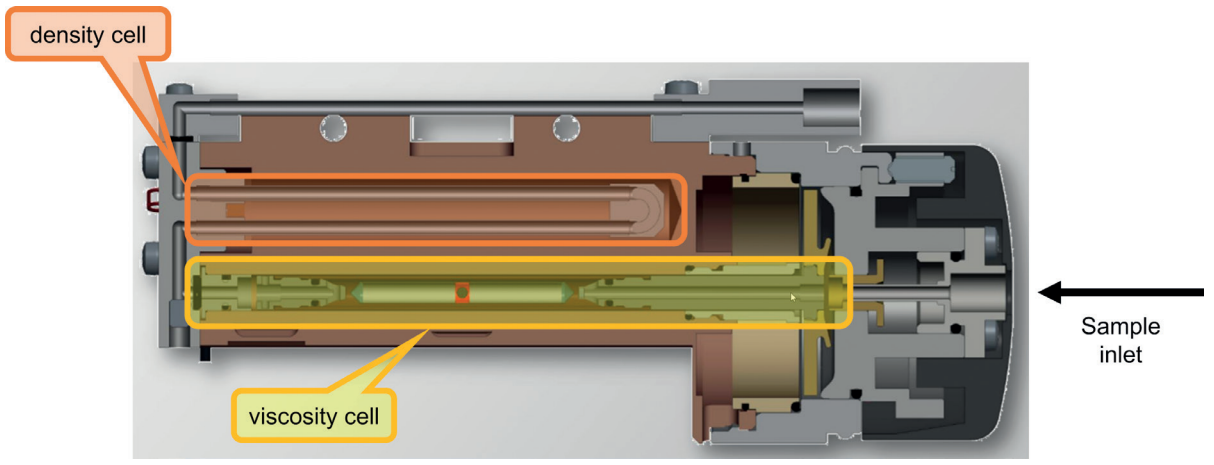


Figure 3: SVM™ measuring cells

Nonetheless, the user must be aware of the following general considerations:

- Bias corrections are only possible if the reference method has a precision statement for the respective sample type and temperature. For instance, ASTM D445 does not include a precision statement for jet fuels at -40 °C. Therefore, although ASTM D7042 does have precision at -40 °C for this sample type, a bias cannot be determined.
- The application of bias corrections does not mean that the numbers will be identical to the reference test method: As previously explained, a bias describes the degree of agreement of the arithmetic means of a large number of test results obtained with both test methods. Hence, individual results obtained from a limited number of measurements on a single apparatus may differ. The numbers are nevertheless valid.

It should be emphasized that the most significant practical aspect of bias corrections is directly stated in ASTM D7042: For the sample types and property ranges studied, the results obtained after the correction may be seen as "practically equivalent" – but, as mentioned, not necessarily identical – to the results from test method ASTM D445. In this way, test method data becomes comparable and, with respect to specifications, conclusions drawn from measurements with either apparatus will be the same. Thus, the user has the possibility to freely choose the desired test method.

Summary

Bias correction formulae are derived from statistical evaluation of the data of inter-laboratory studies by the SDO and serve as a valuable tool to compare measurement data obtained with one test method (in this example ASTM D7042) to results from another method (ASTM D445): After correction, results determined by the new method will be practically equivalent to those of the reference method. Sometimes, the application of such bias corrections is required by specifications. The exact procedure of the calculation is documented in the respective alternate standard and is thus in full compliance with that standard. Bias corrections may be implemented in the instrument software, as is the case with the SVM™ Smart Viscometer, which eliminates the need to perform manual calculations.

The ongoing active development of test methods and specifications by the SDOs is reflected in the precision and bias sections of each test method: Prior to inclusion in a standard, a technical committee usually requests additional data as evidence of the suitability of a particular test method for a new type of specimen. Hence, inter-laboratory studies are initiated and processed, ultimately leading to an expansion of the precision and bias section of the test method itself. This process will continue in the future with novel alternate test methods, and thereby push the adoption of advanced measuring techniques while simplifying everyday lab operations.

If you would like to take part in such development, consider participating in inter-laboratory studies or becoming a member of an SDO. At ASTM in particular, everyone is entitled to participate and actively contribute to such development, for instance, by introducing motions at the respective committees.

References

1. ASTM D445-21e2, "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Cal-culation of Dynamic Viscosity)," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.
2. ASTM D7042-21a, "Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)," Annual Book of ASTM Standards, ASTM International, West Con-shohocken, PA.
3. ISO 5725-1, „ Accuracy (trueness and precision) of measurement methods and results - Part 1: General principles and definitions," International Organization of Standardization, Geneva, Switzerland, 1994.
4. ASTM D396-21, "Standard Specification for Fuel Oils," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.
5. ASTM D975-22, "Standard Specification for Diesel Fuel," Annual Book of ASTM Standards, ASTM International, West Consho-hocken, PA.
6. ASTM D6751-20a, "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels," An-nual Book of ASTM Standards, ASTM International, West Conshohocken, PA.
7. ASTM D7467-20a, "Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20)," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.
8. ASTM D2880-20, "Standard Specification for Gas Turbine Fuel Oils," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.
9. ASTM D1655-22a, "Standard Specification for Aviation Turbine Fuels," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.
10. ASTM D7566 "Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.
11. Joint Inspection Group (JIG) Aviation Fuel Quality Requirements for Jointly Operated Systems, Product Specifica-tions Bulletin 133, Issue 32, November 2020. https://www.jigonline.com/wp-content/uploads/2020/11/Bulletin-133-AFQRJOS-Issue-32-Nov-2020.pdf (accessed: 2022-11-17).
12. DEF STAN 91-091, Revision I14, March 7, 2022 - Turbine Fuel, Kerosene Type, Jet A-1; NATO Code: F-35; Joint Service Designation: AVTUR.
13. ASTM D3699-19 "Standard Specification for Kerosine," Annual Book of ASTM Standards, ASTM International, West Consho-hocken, PA.
14. ASTM D6448-16(2022) "Standard Specification for Industrial Burner Fuels from Used Lubricating Oils," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.
15. ASTM D7666-12(2019) "Standard Specification for Triglyceride Burner Fuel," Annual Book of ASTM Standards, ASTM Interna-tional, West Conshohocken, PA.
16. ASTM D6158-18 "Standard Specification for Mineral Hydraulic Oils," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.
17. "J300 Engine Oil Viscosity Classification." SAE International. 2021.
18. ASTM D2270-10(2016) "Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.

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