The Facts and Figures of Digital Density Measurement

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Density is a fundamental physical property that can be used in conjunction with other properties to characterise both the light and heavy fractions of petroleum and petroleum products. Accurate determination of the density is important because petroleum products, such as fuel oxygenates, are often bought and sold. Therefore, the density value is necessary for the conversion of measured volumes to volumes at the standard temperature of 15.6 °C (60 °F).

For some petroleum products, e.g. automotive spark ignition engine fuel, the density is related to the volumetric energy content. The denser the fuel is, the higher the volumetric energy content. This makes density an important parameter in this field. For other products, such as aviation fuel, density is a measure of fuel mass/unit volume. It is important to know the density in order to calculate fuel load because weight or volume limitations may exist and flight plans must be adjusted to include the fuel density accordingly.

Density and its units

There are three scales in use in the petroleum industry: specific gravity, density and API gravity.

Density is the mass per unit volume at a specified temperature. Specific gravity (sometimes referred to as relative density D t/t) is the ratio of the density of a material at a stated temperature to the density of water at a stated temperature.

API gravity of a fuel oil is based on this formula:

$$API\ Gravity\ [°] = \frac{141.5}{specific\ gravity\ \frac{60}{60}°F} - 131.5$$

This scale is generally used for most transactions in the United States as well as in refinery practice around the world.

ASTM D4052 for petroleum products

In the petroleum industry the determination of density, relative density and API gravity for petroleum distillates and viscous oils by means of a digital density meter is related to one ASTM standard test method – namely the D4052. This standard test method is used for products like gasoline, gasoline-oxygenate blends, diesel, jet fuel, base stocks, waxes and lubricating oils.

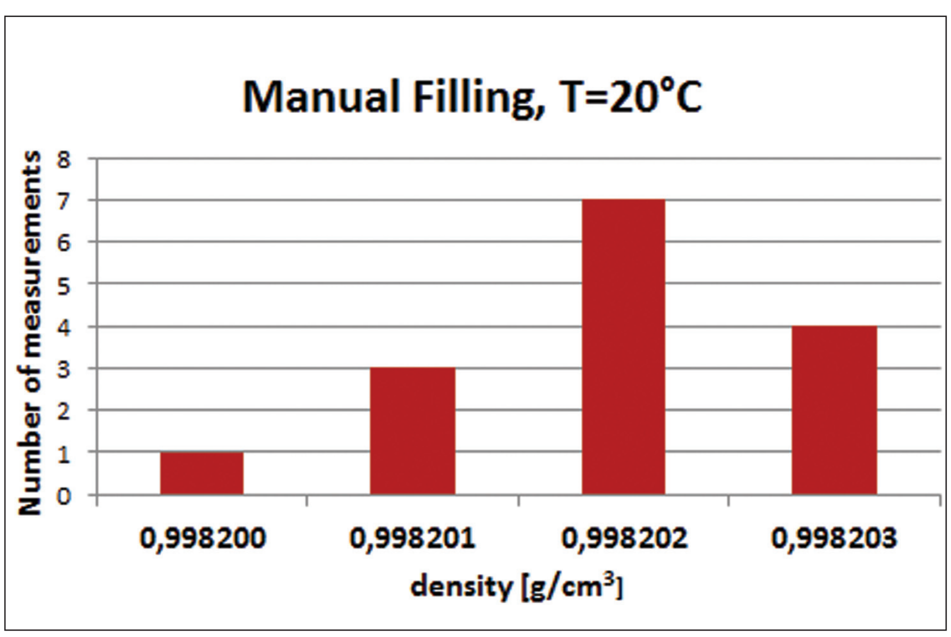

Figure 1: Manual filling of bidistilled water at 20 °C by a syringe (n=15, mean=0.99820193 g/cm^3, STD= 8.8372E-07)

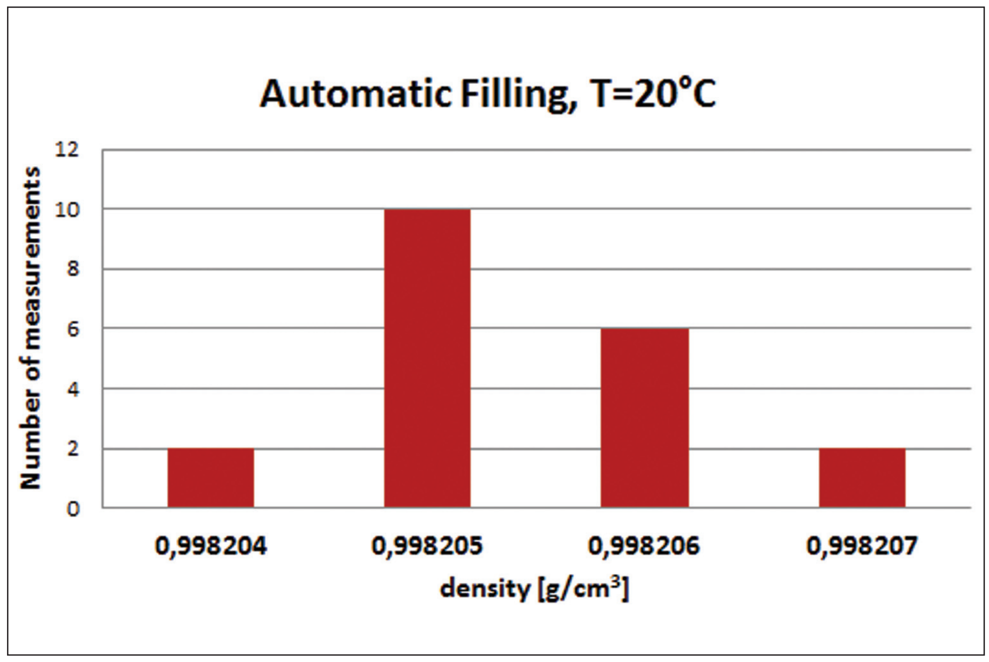

Figure 2: Automatic filling of bidistilled water at 20 °C by an autosampler (n=20; mean= 0.998205 g/cm^3, STD= 8.20783E-07)

Filling according to D4052

ASTM D4052 specifies two different ways of sample injection: manual injection (Fig. 1) and automated injection (Fig. 2). For manual injection, a small amount of sample (1 to 2 mL) is introduced into the clean and dry U-tube using a suitable syringe or alternatively by using a flow-through or pressure adapter. For automated injection, the sample is introduced by an autosampler. When an autosampler is used for the determination of density of gasoline and RFG, the ASTM standard requires analysis of two separate test specimens per sample. In both cases of injection it has to be ensured that the U-tube is properly filled and that no gas bubbles are present. This is done by using optical or physical methods[1]. An example of an optical method is an inspection window or a camera which shows the image of the entire U-tube (Fig. 3). The camera image of the whole U-tube is stored for later verification, if needed. In contrast physical methods determine the absence or presence of a gas bubble automatically by evaluating the measuring cell's period of oscillation during the measurement. This innovative technology ensures highly repeatable results and eliminates operator-induced influences on the measurement e.g. bubbles in dark samples – not visible to the human eye – are automatically detected by the instrument itself. Density meters which combine both physical and optical methods ensure the highest level of correctness and accuracy of the results.

Bubbles: detection required

At first sight, avoiding bubbles by placing the U-tube in a vertical position seems very promising due to the fact that air bubbles escape due to buoyancy. However, it is known that air bubbles cannot escape from viscous samples in the required time and consequently they influence the measurement. Therefore, the position of the U-tube - whether vertical or horizontal - does not play a significant role in reducing the influence of bubbles on the results. An important consideration when detecting bubbles is the time that is needed for the density meter to alert the operator that bubbles are present in the sample. The most accurate density meters on the market give this warning within 2 minutes, whereas other instruments give this information only after 13 minutes. A fast warning saves the operator time and allows immediate measurement of a subsequently correctly filled sample.

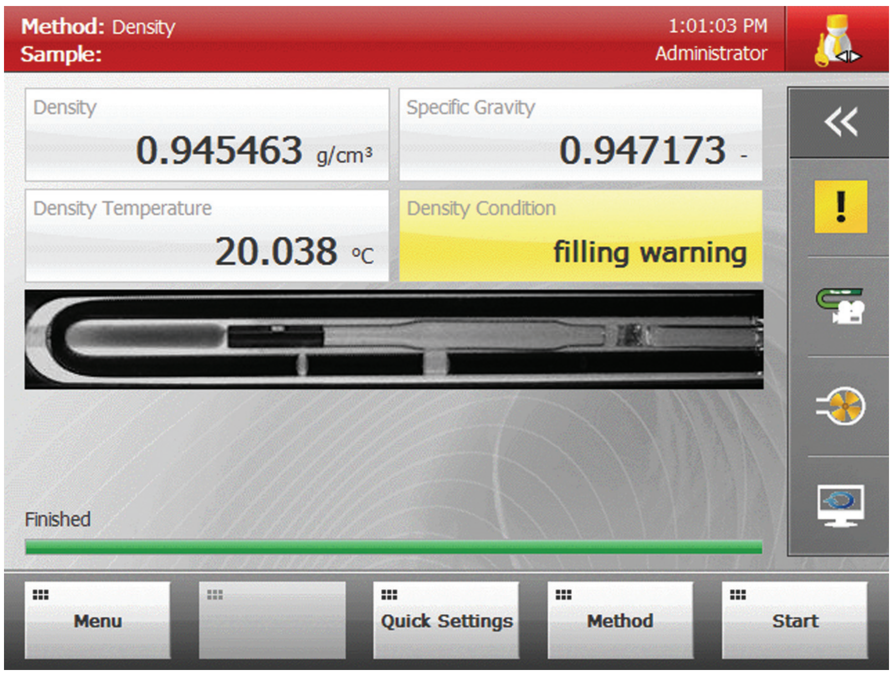

Figure 3: Screen of an "intelligent" density meter including a camera image of the U-tube and filling warning due to the bubbles in the sample

The choice of autosampler

Whether to use an autosampler in QC laboratories in the petroleum industry depends on the number of samples, the physical properties of the sample and the total amount of instruments operated by a single user in the laboratory.

Flexibility and freedom of choice are given by systems which allow an upgrade of the density meter with an autosampler at a later date, e.g. should the need arise due to low repeatability of results or increasing numbers of samples. In cases of dispute, the referee method requires samples to be introduced manually by means of a syringe, flow-through or pressure adapter. For these cases, a density meter which can also be filled by manual injection is an asset.

What about crude oils?

For all crude oils that can be handled in a normal fashion at test temperatures between 15 °C and 35 °C the ASTM standard test method for density and relative density by a digital density analyzer is D5002. Filling of crude oils according to D5002 is performed by a syringe. In this case, the syringe has to be left in place and the sample outlet has to be plugged[2]. During filling, the operator checks for bubbles in the U-tube through the inspection window and/or on the camera image (Fig. 3). If the dark color of the sample makes observation of air or gas bubbles very difficult, the operator can detect bubbles by observing the density value and looking for possible fluctuations. Otherwise, an "intelligent" density meter can use a physical method to detect bubbles (Fig. 3) during measurement. This "intelligence" gives the operator the secure knowledge that the visual inspection was correct. The stored data is also useful as evidence for later verification.

For the optical inspection a transparent U-tube is necessary, ideally made out of borosilicate glass. Any non-transparent U-tube material such as stainless steel is not appropriate for the density measurement of crude oil according to D5002.

Removing the influence of temperature

The temperature has an important influence on the density: the outcome of a temperature difference of 0.1 °C results in a density error of up to 0.0001 g/cm³ (depending on the nature of the sample). An accurate density measurement requires accurate temperature determination and good temperature stability, whereby the speed at which the measuring cell adjusts to temperature is irrelevant. In other words, the material of the U-tube does not have any bearing on the accuracy of the density measurement. During a routine day in a QC lab in the petroleum industry, different types of samples - from jet fuel to waxes - have

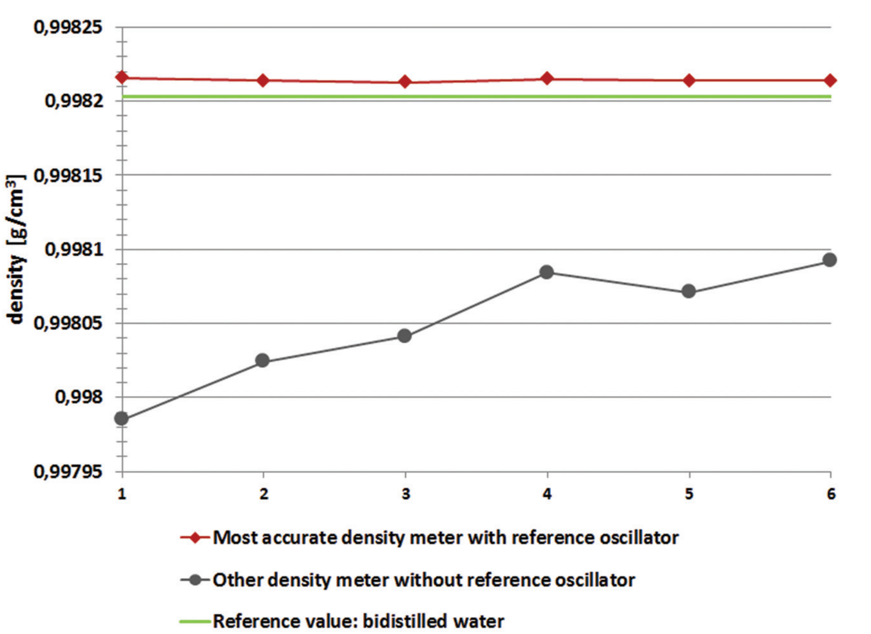

Figure 4: Density readings at 20 °C (after measurements at 80 °C) of two different density meter models, one with and one without integrated reference oscillator

to be analysed at different test temperatures. Therefore, the density meter either has to be calibrated at each temperature or else the adjustment covers the whole temperature range of the instrument due to a special design. To achieve adjustment over the whole temperature range via special design, using an integrated reference oscillator[3] has proven to be the most suitable and accurate approach (Fig. 4).

The viscosity requires correction

With increasing viscosity of the sample the density increases due to translational and rotational movements in the sample during the oscillation[4] in the U-tube. A typical viscosity influence can be seen in figure 5. The maximum error of a typical U-tube is 6x10-4 g/cm³ for a viscosity higher than 500 m.Pa.s. In some density meters on the market this density error based on the viscosity is compensated by the instrument itself and the user does not need to know the viscosity of the sample. This automatic correction reduces the bias and gives the operator peace of mind to measure the true density value of any petroleum sample within the entire viscosity range (Fig. 6).

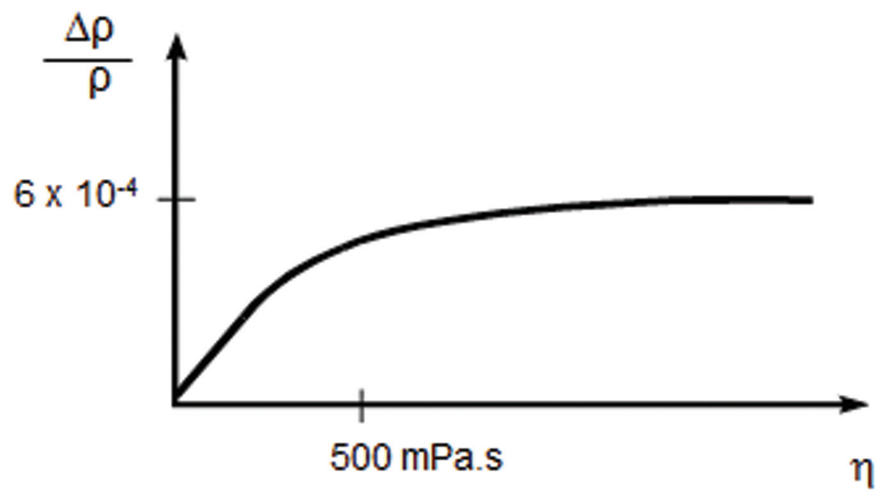

Figure 5: Viscosity influence on the density measurement based on the oscillating U-tube principle

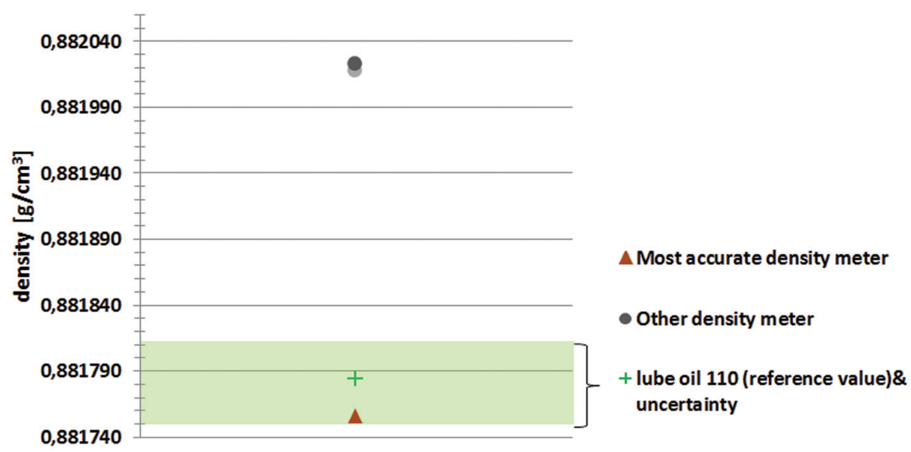

Figure 6: Deviation of measured density values of lube oil 110 (as the viscous standard reference) measured on 2 different density meter models

Conclusion

For the petroleum industry, two ASTM standards specify conditions for density measurement in the lab by means of a digital density meter. These are ASTM D4052 for petroleum products and lubricating oils, and ASTM D5002 for crude oils. ASTM D4052 allows use of an autosampler. However, in cases of dispute, it is necessary to follow the referee method which requires manual filling.

To achieve accurate density results with minimum effort, it is also useful to have a density meter which provides automatic viscosity correction and full-range temperature adjustment. Density meters with a reference oscillator need only one density adjustment to provide density results across the whole range of measuring temperatures.

The advantage of borosilicate glass oscillating U-tube density meters is that the sample is visible for observing the filling process and therefore any gas or air bubbles can be seen. With high-end density meters, an intelligent bubble detection feature (physical method) serves as additional verification of bubble-free filling. Density meters providing these state-of-the-art measuring technologies provide utmost levels of reliability, accuracy as well as assistance to operators dealing with many different measurements at one time.

References:

(1) D4052: Standard test method for Density, Relative Density and API Gravity of Liquids by Digital Density Meter

(2) D5002: Density and Relative Density of Crude Oils by Digital Density Analyzer

(3) Pat.No. AT 399051

(4) Hans Stabinger, Density Measurement Using Modern Oscillating Transducers, South Yorkshire Trading Unit, Sheffield, 1994