



Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer¹

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1. Scope

1.1 This test method covers the determination of the density or relative density of crude oils that can be handled in a normal fashion as liquids at test temperatures between 15 and 35°C. This test method applies to crude oils with high vapor pressures provided appropriate precautions are taken to prevent vapor loss during transfer of the sample to the density analyzer.

1.2 This test method was evaluated in round robin testing using crude oils in the 0.75 to 0.95 g/mL range. Lighter crude oil can require special handling to prevent vapor losses. Heavier crudes can require measurements at higher temperatures to eliminate air bubbles in the sample.

1.3 The accepted units of measurement of density are grams per millilitre and kilograms per cubic metre.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in 7.4, 7.5, and 7.6.

2. Referenced Documents

2.1 ASTM Standards:

- D 941 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Lipkin Bicapillary Pycnometer²
- D 1193 Specification for Reagent Water³
- D 1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer²
- D 1250 Guide for Petroleum Measurement Tables²
- D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter⁴
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products⁴
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products⁴

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.OD on Physical Methods.

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² *Annual Book of ASTM Standards*, Vol 05.01.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 05.02.

D 4377 Test Method for Water in Crude Oils by Volumetric Karl Fischer Titration⁴

3. Terminology

3.1 Definitions:

3.1.1 *density*—mass per unit volume at a specified temperature.

3.1.2 *relative density*—the ratio of the density of a material at a stated temperature to the density of water at a stated temperature.

4. Summary of Test Method

4.1 Approximately 0.7 mL of crude oil sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.

5. Significance and Use

5.1 Density is a fundamental physical property that can be used in conjunction with other properties to characterize the quality of crude oils.

5.2 The density or relative density of crude oils is used for the conversion of measured volumes to volumes at the standard temperatures of 15°C or 60°F and for the conversion of crude mass measurements into volume units.

5.3 The application of the density result obtained from this test method, for fiscal or custody transfer accounting calculations, can require measurements of the water and sediment contents obtained on similar specimens of the crude oil parcel.

6. Apparatus

6.1 *Digital Density Analyzer*—A digital analyzer consisting of a U-shaped, oscillating sample tube and a system for electronic excitation, frequency counting, and display. The analyzer must accommodate the accurate measurement of the sample temperature during measurement or must control the sample temperature as described in 6.2 and 6.5. The instrument shall be capable of meeting the precision requirements described in Test Method D 4052.

6.2 *Circulating Constant-Temperature Bath*, capable of maintaining the temperature of the circulating liquid constant to $\pm 0.05^\circ\text{C}$ in the desired range. Temperature control can be maintained as part of the density analyzer instrument package.

6.3 *Syringes*, at least 2 mL in volume with a tip or an adapter tip that will fit the inlet of the density analyzer.

6.4 *Flow-Through or Pressure Adapter*, for use as an alternative means of introducing the sample into the density meter.

6.5 *Thermometer*, calibrated and graduated to 0.1°C, and a thermometer holder that can be attached to the instrument for setting and observing the test temperature. In calibrating the thermometer, the ice point and bore corrections should be estimated to the nearest 0.05°C. Precise setting and control of the test temperature in the sample tube is extremely important. An error of 0.1°C can result in a change in density of one in the fourth significant figure.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

7.3 *Water*, redistilled, freshly boiled and cooled reagent water for use as a primary calibration standard.

7.4 *Acetone*, for flushing and drying the sample tube. (**Warning:** Extremely flammable.)

7.5 *Petroleum Naphtha*,⁶ for flushing viscous petroleum samples from the sample tube. (**Warning:** Extremely flammable.)

7.6 *n-Nonane, n-tridecane or cyclohexane*, 99 % purity or better, or similar pure material for which the density is known precisely from literature references or by direct determination in accordance with Test Method D 941 or D 1217. (**Warning:** Extremely flammable.)

8. Sampling, Test Specimens, and Test Units

8.1 Sampling is defined as all the steps required to obtain an aliquot of the contents of any pipe, tank or other system, and to place the sample into the laboratory test container. The laboratory test container and sample volume shall be of sufficient dimensions to allow mixing as described in 8.3.1. Mixing is required to obtain a homogeneous sample for analysis.

8.2 *Laboratory Sample*—Use only representative samples obtained as specified in Practices D 4057 or D 4177 for this test method.

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

⁶ Suitable solvent naphthas are marketed under various designations such as “petroleum ether,” “ligroine,” or “precipitation naphtha.”

8.3 *Test Specimen*—The aliquot of sample obtained from the laboratory sample and delivered to the density analyzer sample tube. The test specimen is obtained as follows:

8.3.1 Mix the sample of crude oil to homogenize any sediment and water present. The mixing may be accomplished as described in Practice D 4177 or Test Method D 4377. Mixing at room temperature in an open container can result in the loss of light ends, so mixing in closed, pressurized containers or at sub-ambient temperatures is recommended.

8.3.2 Draw the test specimen from a properly mixed laboratory sample using an appropriate syringe. Alternatively, if the proper density analyzer attachments and connecting tubes are used then the test specimen can be delivered directly to the analyzer’s sample tube from the mixing container.

9. Preparation of Apparatus

9.1 Set up the density analyzer and constant temperature bath following the manufacturer’s instructions. Adjust the bath or internal temperature control so that the desired test temperature is established and maintained in the sample compartment of the analyzer. Calibrate the instrument at the same temperature at which the density of the sample is to be measured.

10. Calibration of Apparatus

10.1 Calibrate the instrument when first setting up and whenever the test temperature is changed. Thereafter, conduct calibration checks at least weekly during routine operation or more frequently as may be dictated by the nature of the crude oils being measured, (see 10.3).

10.2 Initial calibration, or calibration after a change in test temperature, necessitates calculation of the values of the Constants A and B from the periods of oscillation, (T), observed when the sample cell contains certified reference liquids such as air and double-distilled boiled water. Other calibrating materials such as *n*-nonane, *n*-tridecane, cyclohexane, and *n*-hexadecane (for high temperature applications) can also be used as appropriate.

10.2.1 While monitoring the oscillator period, T , flush the sample tube with petroleum naphtha, followed with an acetone flush and dry with dry air. Continue drying until the display exhibits a steady reading. In cases where saline components can be deposited in the cell, flush with distilled water followed by acetone and dry air. Contaminated or humid air can affect the calibration. When these conditions exist in the laboratory, pass the air used for calibration through a suitable purification and drying train. In addition, the inlet and outlet ports for the U-tube must be plugged during measurement of the calibration air to prevent ingress of moist air.

10.2.2 Allow the dry air in the U-tube to come to thermal equilibrium with the test temperature and record the T -value for air.

10.2.3 Introduce about 0.7 mL of freshly boiled and cooled double-distilled water into the sample tube from the bottom opening using a suitable syringe. The water must be free of even the smallest air or gas bubbles. The sample tube shall be completely full. Allow the water to reach thermal equilibrium at the test temperature and record the T -value for water and the test temperature.

10.2.4 Alternatively introduce one of the hydrocarbon calibration standards and measure the T -value as in 10.2.3.

10.2.5 Calculate the density of air at the temperature of test using the following equation:

$$d_a = 0.001293[273/T][P/760] \text{ g/mL} \quad (1)$$

where:

T = temperature, K, and

P = barometric pressure, torr.

10.2.6 Determine the density of water at the temperature of test by reference to Table 1.

10.2.7 Alternatively record the density at the test temperature for the hydrocarbon calibrant used in 10.2.4 as obtained from an appropriate reference source or from direct determination (see 7.6).

10.2.8 Using the observed T -values and the reference values for water and air, calculate the values of the Constants A and B using the following equations:

$$A = [T_w^2 - T_a^2][d_w - d_a] \quad (2)$$

$$B = T_a^2 - (A \times d_a) \quad (3)$$

where:

T_w = observed period of oscillation for cell containing water,

T_a = observed period of oscillation for cell containing air,

d_w = density of water at test temperature, and

d_a = density of air at test temperature.

Alternatively, use the T and d values for the other reference liquid if one is used.

10.2.9 If the instrument is equipped to calculate density from the Constants A and B and the observed T -value from the sample, then enter the constants in the instrument memory in accordance with the manufacturer's instructions.

10.2.10 Check the calibration and adjust if needed by performing the routine calibration check described in 10.3.

10.2.11 To calibrate the instrument to determine relative density, that is, the density of the sample at a given temperature referred to the density of water at the same temperature, follow 10.2.1-10.2.9, but substitute 1.000 for d_w in performing the calculations described in 10.2.8.

10.3 Since some crude oils can be difficult to remove from the sample tube, frequent calibration checks are recommended. These checks and any subsequent adjustments to Constants A

and B can be made if required, without repeating the calculation procedure.

NOTE 1—The need for a change in calibration is generally attributable to deposits in the sample tube that are not removed by the routine flushing procedure. Although this condition can be compensated for by adjusting A and B, as described below, it is good practice to clean the tube with warm chromic acid solution (**Warning**—Causes severe burns. A recognized carcinogen.) whenever a major adjustment is required. Chromic acid solution is the most effective cleaning agent; however, surfactant-type cleaning fluids have also been used successfully.

10.3.1 Flush and dry the sample tube as described in 10.2.1 and allow the display to reach a steady reading. If the display does not exhibit the correct T -value or density for air at the temperature of test, repeat the cleaning procedure or adjust the value of Constant B commencing with the last decimal place until the correct density is displayed.

10.3.2 If adjustment to Constant B was necessary in 10.3.1 then continue the recalibration by introducing freshly boiled and cooled double-distilled water into the sample tube as described in 10.2.3 and allowing the display to reach a steady reading. If the instrument has been calibrated to display the density, adjust the reading to the correct value for water at the test temperature, (see Table 1) by changing the value of Constant A, commencing with the last decimal place. If the instrument has been calibrated to display the relative density, adjust the reading to the value 1.0000.

NOTE 2—In applying this periodic calibration procedure, it has been found that more than one value each for A and B, differing in the fourth decimal place, will yield the correct reading for the density of air and water. The setting chosen would then be dependent upon whether it was approached from a higher or lower value. The setting selected by this method could have the effect of altering the fourth place of the reading obtained for a sample.

10.4 Some analyzer models are designed to display the measured period of oscillation only (T -values) and their calibration requires the determination of an instrument constant K, that must be used to calculate the density or relative density from the observed data. Use the procedure in 10.4.1, 10.4.2 and 10.4.3 in this case.

10.4.1 Flush and dry the sample tube as described in 10.2.1 and allow the air to reach equilibrium at the test temperature and the readout to display a steady value. Record the T -value for air.

10.4.2 Introduce freshly boiled and cooled double-distilled water into the sample tube as described in 10.2.3, allow the display to reach a steady reading and record the T -value for water.

10.4.3 Using the observed T -values and the reference values for water and air (10.2.5 and 10.2.6), calculate the instrument constant, K , using the following equations:

for density:

$$K_1 = [d_w - d_a][T_w^2 - T_a^2] \quad (4)$$

for relative density:

$$K_2 = [1.0000 - d_a][T_w^2 - T_a^2] \quad (5)$$

where:

TABLE 1 Density of Water^A (in vacuo)

Temperature, °C	Density, g/mL	Temperature, °C	Density, g/mL	Temperature, °C	Density, g/mL
0.0	0.999840	21.0	0.997991	40.0	0.992212
3.0	0.999964	22.0	0.997769	45.0	0.990208
4.0	0.999964	23.0	0.997537	50.0	0.988030
5.0	0.999964	24.0	0.997295	55.0	0.985688
10.0	0.999699	25.0	0.997043	60.0	0.983191
15.0	0.999099	26.0	0.996782	65.0	0.980546
15.56	0.999012	27.0	0.996511	70.0	0.977759
16.0	0.998943	28.0	0.996231	75.0	0.974837
17.0	0.998774	29.0	0.995943	80.0	0.971785
18.0	0.998595	30.0	0.995645	85.0	0.968606
19.0	0.998404	35.0	0.994029	90.0	0.965305
20.0	0.998203	37.78	0.993042	100.0	0.958345

^ADensities conforming to the International Temperature Scale 1990 (ITS 90) were extracted from Appendix G, *Standard Methods for Analysis of Petroleum and Related Products 1991*, Institute of Petroleum, London.

T_w = observed period of oscillation for cell containing water,

T_a = observed period of oscillation for cell containing air,

d_w = density of water at test temperature, and

d_a = density of air at test temperature.

11. Procedure

11.1 Introduce about 0.7 mL of crude oil into the clean, dry, sample tube of the instrument using a suitable syringe. Leave the syringe in place and plug the exit port.

11.2 Turn on the illumination light and examine the sample tube carefully. Make sure that there is no obvious presence of bubbles trapped in the U-tube, and that it is filled completely. The sample must appear to be homogeneous. Turn the illumination light off immediately after inspection of the sample tube, since the heat generated affects the measurement temperature.

11.3 Allow the sample to equilibrate to the test temperature before proceeding to evaluate the test sample for the presence of unseen air or gas bubbles.

11.4 For dark crude oil samples the observation of air or gas bubbles in the sample tube is very difficult. The presence of bubbles can often be detected, however, by observing the fluctuations of the digital display of the T -value or density value. Air or gas bubbles cause large random variations in the third and fourth significant figures for density reading and fifth and sixth significant figures for T readings. When bubbles are absent and the sample is at equilibrium with the test temperature, the displayed values are stable, do not drift, and show only small variations of the order of ± 1 to 2 units in the last significant figure. If stable values are not observed after a few minutes, then repeat the injection of a new sample into the tube.

NOTE 3—When viscous liquids are being measured, a stable reading can be achieved even when air or gas bubbles are present. Careful injection of fresh sample will often eliminate bubbles. Since bubbles contribute to lower density readings, an observed increase in the density of the liquid after injection of fresh sample tends to suggest that bubbles were previously present.

11.5 After the instrument displays a steady reading to four significant figures for density and five for T -values, indicating that temperature equilibrium has been reached, record the density or T -value.

11.6 Flush and dry the sample tube as described in 10.2.1 and check the calibration as described in 10.3.1 prior to introducing another sample.

12. Calculation

12.1 *Calculating Density Analyzers*— The recorded value is the final result, expressed either as density in g/mL, kg/m³ or as relative density. Note that kg/m³ = 1000 × g/mL.

12.2 *Noncalculating Density Analyzers*— Using the observed T -value for the sample and the T -value for water and appropriate instrument constants determined in 10.4.3, calculate the density or relative density using Eq 6 and Eq 7. Carry out all calculations to six significant figures and round the final results to four. Note that kg/m³ = 1000 × g/mL.

for density:

$$\text{density, g/mL at } t = d_w + K_1(T_s^2 - T_w^2) \quad (6)$$

for relative density:

$$\text{relative density, } t/t = 1 + K_2(T_s^2 - T_w^2) \quad (7)$$

where:

T_w = observed period of oscillation for cell containing water,

T_s = observed period of oscillation for cell containing sample,

d_w = density of water at test temperature,

K_1 = instrument constant for density,

K_2 = instrument constant for relative density, and

t = temperature of test °C.

12.3 If it is necessary to convert a result obtained using the density analyzer to a density or relative density at another temperature, Guide D 1250 can be used only if the table values have not been corrected for the glass expansion factor.

13. Report

13.1 In reporting density, give the test temperature and the units, (for example: density at 20°C = 0.8765 g/mL or 876.5 kg/m³ (in vacuo)).

13.2 In reporting relative density, give both the test temperature and the reference temperature, but no units, (for example: relative density, 15/15°C = x.xxxx).

13.3 Report the final result to four significant figures.

14. Precision and Bias^{7,8}

14.1 The precision of this test method as obtained by statistical examination of interlaboratory test results at test temperatures of 15 and 20°C is as follows:

14.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method, exceed the following value only in one case in twenty, (see Table 2):

range	repeatability
0.75 to 0.95	0.00105X

where:

X = sample mean.

14.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in

⁷ Supporting data are available from ASTM Headquarters, Request RR:D02-1257.

⁸ Biased results for high viscosity samples (>ca. 100 mPa-s dynamic viscosity) has been reported in the literature. For additional information, consult the *Journal of Physical Chemistry*, Vol 84, 1980, pp. 158–162 and the *Journal of the Chemical Society Faraday Translation*, Vol 86 (1), 1990, pp. 145–149.

TABLE 2 Precision Values

Density	Repeatability	Reproducibility
0.70	0.0007	0.0029
0.75	0.0008	0.0031
0.80	0.0008	0.0033
0.85	0.0009	0.0035
0.90	0.0009	0.0037
0.95	0.0010	0.0039

the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty, (see Table 2):

range	reproducibility
0.75 to 0.95	0.00412X

where:

X = sample mean.

14.2 *Bias*—After suggestions of its existence from literature⁹, a study has been performed which has confirmed the presence of a bias between known density values for reference materials and from values determined according to this test

method on the same reference materials. The matrix for this bias study comprised 15 participants, each analyzing four reference oils with certified density values, established by the Netherlands Meet Instituut (NMI), by pycnometry, covering densities in the range of 747 to 927 kg/m³ at 20°C, with viscosities between 1 and 5000 mPa.s (also at 20°C). This study is documented in ASTM Research Report RR: D02–1387. Method users should, therefore, be aware that results obtained by this test method can be biased by as much as 0.6 kg/m³ (0.0006 g/mL).

15. Keywords

15.1 density; relative density; digital density analyzer; crude oils

⁹Fitzgerald, H. and D., “An Assessment of Laboratory Density Meters,” *Petroleum Review*, November 1992, pp. 544–549.

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