

DOCKET NO. SA 516

EXHIBIT NO. 8H

**NATIONAL TRANSPORTATION SAFETY BOARD**

**WASHINGTON, D.C.**

ASTM STANDARD D4052: "STANDARD TEST METHOD FOR  
DENSITY AND RELATIVE DENSITY OF LIQUIDS BY DIGITAL  
DENSITY METER."

by

Gordon J. Hookey



## Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter<sup>1</sup>

This standard is issued under the fixed designation D 4052; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This method was adopted as a joint ASTM-IP standard in 1984.*

### 1. Scope

1.1 This test method covers the determination of the density or relative density of petroleum distillates and viscous oils that can be handled in a normal fashion as liquids at test temperatures between 15 and 35°C. Its application is restricted to liquids with vapor pressures below 600 mm Hg (80 kPa) and viscosities below about 15 000 cSt (mm<sup>2</sup>/s) at the temperature of test.

1.2 This test method should not be applied to samples so dark in color that the absence of air bubbles in the sample cell cannot be established with certainty. For the determination of density in crude oil samples use Test Method D 5002.

1.3 The accepted units of measure for density are grams per millilitre or 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.* For specific hazard statements, see Notes 1 and 2.

### 2. Referenced Document

#### 2.1 ASTM Standard:

D 1193 Specification for Reagent Water<sup>2</sup>

D 1250 Guide for Petroleum Measurement Tables<sup>3</sup>

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>4</sup>

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products<sup>4</sup>

D 4377 Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration<sup>4</sup>

D 5002 Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer<sup>5</sup>

### 3. Terminology

#### 3.1 Definitions:

<sup>1</sup> 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 on Hydrocarbon Analysis.

Current edition approved Jan. 15, 1995. Published March 1995. Originally published as D 4052 - 81. Last previous edition D 4052 - 91.

<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 05.01.

<sup>4</sup> Annual Book of ASTM Standards, Vol 05.02.

<sup>5</sup> Annual Book of ASTM Standards, Vol 05.03.

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 A small volume (approximately 0.7 mL) of liquid 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 both the light and heavy fractions of petroleum and petroleum products.

5.2 Determination of the density or relative density of petroleum and its products is necessary for the conversion of measured volumes to volumes at the standard temperature of 15°C.

### 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. The instrument shall be capable of meeting the precision requirements described in this test method.

6.2 *Circulating Constant-Temperature Bath*, (optional) 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 opening of the oscillating tube.

6.4 *Flow-Through or Pressure Adapter*, for use as an alternative means of introducing the sample into the density analyzer either by a pump or by vacuum.

6.5 *Thermometer*, calibrated and graduated to  $0.1^\circ\text{C}$ , 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 connections should be estimated to the nearest 0.05°C.

## 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.<sup>6</sup> 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 *Petroleum Naphtha*,<sup>7</sup> for flushing viscous petroleum samples from the sample tube.

NOTE 1—Extremely flammable.

7.5 *Acetone*, for flushing and drying the sample tube.

NOTE 2: **Warning**—Extremely flammable.

7.6 *Dry Air*—for blowing the oscillator tube.

## 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 capacity to mix the sample and 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.

8.3 *Test Specimen*—A portion or volume 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 if required to homogenize. The mixing may be accomplished as described in Practice D 4177 (Section 11) or Test Method D 4377 (A.1). Mixing at room temperature in an open container can result in the loss of volatile material, 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.

NOTE 3: **Caution**—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 decimal.

## 10. Calibration of Apparatus

10.1 Calibrate the instrument when first set up and whenever the test temperature is changed. Thereafter, conduct calibration checks at weekly intervals during routine operation.

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 air and redistilled, freshly boiled and cooled reagent 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. 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 a small volume (about 0.7 mL) of redistilled, freshly boiled and cooled reagent water into the sample tube from the bottom opening using a suitable syringe. The test portion must be homogeneous and free of even the smallest air or gas bubbles. The sample tube does not have to be completely full as long as the liquid meniscus is beyond the suspension point. Allow the display to reach a steady reading and record the *T*-value for water.

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

$$d_a, \text{ g/mL} = 0.001293[273.15/T][P/760] \quad (1)$$

where:

*T* = temperature, K, and

*P* = barometric pressure, torr.

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

10.2.6 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<sub>w</sub>* = observed period of oscillation for cell containing water,

*T<sub>a</sub>* = observed period of oscillation for cell containing air,

*d<sub>w</sub>* = density of water at test temperature, and

<sup>6</sup> *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

<sup>7</sup> Suitable solvent naphthas are marketed under various designations such as "Petroleum Ether," "Ligroine," or "Precipitation Naphtha."

$d_a$  = density of air at test temperature.

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

10.2.7 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.

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

10.2.9 To calibrate the instrument to display relative density, that is, the density of the sample at a given temperature referred to the density of water at the same temperature, follow sections 10.2.1 through 10.2.7, but substitute 1.000 for  $d_w$  in performing the calculations described in 10.2.6.

10.3 Weekly calibration adjustments to constants  $A$  and  $B$  can be made if required, without repeating the calculation procedure.

NOTE 4—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  $B$ , 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 cleaning fluids have also been used successfully.

10.3.1 Flush and dry the sample tube as described in 9.2.1 and allow the display to reach a steady reading. If the display does not exhibit the correct 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 redistilled, freshly boiled and cooled reagent water into the sample tube as described in 10.2.3 and allow 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 (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 5—In applying this weekly calibration procedure, it can be found that more than one value each for  $A$  and  $B$ , differing in the fourth decimal place, will yield the correct density 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  $K$ , which must be used to calculate the density or relative density from the observed data.

10.4.1 Flush and dry the sample tube as described in 10.2.1 and allow the display to reach a steady reading. Record the  $T$ -value for air.

10.4.2 Introduce redistilled, freshly boiled and cooled reagent 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 (10.2.4 and 10.2.5), 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:

$T_w$  = 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 a small amount (about 0.7 mL) of sample into the clean, dry sample tube of the instrument using a suitable syringe.

11.2 The sample can also be introduced by siphoning. Plug the external TFE-fluorocarbon capillary tube into the lower entry port of the sample tube. Immerse the other end of the capillary in the sample and apply suction to the upper entry port using a syringe or vacuum line until the sample tube is properly filled.

11.3 Turn on the illumination light and examine the sample tube carefully. Make sure that no bubbles are trapped in the tube, and that it is filled to just beyond the suspension point on the right-hand side. The sample must be homogeneous and free of even the smallest bubbles.

NOTE 6—If the sample is too dark in color to determine the absence of bubbles with certainty, the density cannot be measured within the stated precision limits of Section 14.

11.4 Turn the illumination light off immediately after sample introduction, because the heat generated can affect the measurement temperature.

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.

## 12. Calculation

12.1 *Calculating Density Analyzers*—The recorded value is the final result, expressed either as density in g/mL, kg/m<sup>3</sup> or as relative density. Note that kg/m<sup>3</sup> = 1000 × g/mL.

TABLE 1 Density of Water<sup>A</sup>

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	0.999972	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	0.958345

<sup>A</sup> Densities 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.

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 Eqs 6 and 7. Carry out all calculations to six significant figures and round the final results to four.

For density:

$$\text{density, g/mL (kg/dm}^3\text{) at } t = d_w + K_1(T_s^2 - T_w^2) \quad (6)$$

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 meter to a density or relative density at another temperature, Guide D 1250 can be used only if the glass expansion factor has been excluded.

### 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/m<sup>3</sup>).

13.2 In reporting relative density, give both the test tem-

perature and the reference temperature, but no units (for example: relative density, 20/20°C = 0.xxxx).

13.3 Report the final result to the fourth decimal place.

### 14. Precision and Bias

14.1 The precision of the 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 the test method, exceed the following value only in one case in twenty:

Range	Repeatability
0.68–0.97 g/mL	0.0001

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

Range	Reproducibility
0.68–0.97 g/mL	0.0005

14.2 *Bias*—The accuracy of results shall not differ from the established value by more than 0.0005 g/mL when compared to pure reference material. Specific bias has not been established by cooperative testing.

### 15. Keywords

15.1 density; digital density analyzer; petroleum distillates; petroleum products; relative density

*The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.*