INTERNATIONAL STANDARD

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Crude petroleum and petroleum products — Determination of density — Oscillating U-tube method

Pétroles bruts et produits pétroliers — Détermination de la masse volumique — Méthode du tube en U oscillant

Reference number
ISO 12185:1996(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 12185 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*, Subcommittee SC 3, *Static petroleum measurement*.

Annex A forms an integral part of this International Standard. Annex B is for information only.

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Crude petroleum and petroleum products — Determination of density — Oscillating U-tube method

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems 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.

1 Scope

This International Standard specifies a method for the determination, using an oscillating U-tube density meter, of the density of crude petroleum and related products within the range 600 kg/m^3 to 1 100 kg/m^3 which can be handled as single-phase liquids at the test temperature and pressure.

This International Standard is applicable to liquids of any vapour pressure as long as suitable precautions are taken to ensure that they remain in single phase with no loss of light ends and subsequent changes in composition and density during both the sample handling and the density determination.

NOTE 1 If the determined density is to be converted to a density at some reference temperature using petroleum measurement tables, the determination should be carried out at a temperature as close as possible to the reference temperature in order to minimize uncertainties due to the use of generalized tables.

This method is not intended for use in calibrating on-line density meters.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 91-1:1992, *Petroleum measurement tables — Part 1: Tables based on reference temperatures of 15 °C and 60 degrees F.*

ISO 91-2:1991, *Petroleum measurement tables — Part 2: Tables based on a reference temperature of 20 °C.*

ISO 3015:1992, *Petroleum products — Determination of cloud point.*

ISO 3016:1994, *Petroleum products — Determination of pour point.*

ISO 3170:1988, *Petroleum liquids — Manual sampling.*

ISO 3171:1988, *Petroleum liquids — Automatic pipeline sampling.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 3838:1983, *Crude petroleum and liquid or solid petroleum products — Determination of density or relative density — Capillary-stoppered pyknometer and graduated bicapillary pyknometer methods.*

IP[1] 389/93, *Determination of wax appearance temperature of middle distillate fuels by differential thermal analysis or differential scanning calorimetry.*

IP 1995, *Standard methods for analysis and testing of petroleum and related products,* Appendix G *Density of water;* Appendix H *Density of ambient air.*

BIPM[2] Tables, *Density of water* and *Density of ambient air,* to replace, when published, the corresponding IP tables.

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 density: Mass of the substance, expressed in kilograms, divided by its volume, expressed in cubic metres.

3.2 reference temperature: Temperature at which the sample density is to be reported.

NOTE 2 This temperature should be either 15 °C or 20 °C.

4 Principle

A small (typically less than 1 ml) portion of the test sample is introduced into a temperature-controlled sample cell. The oscillation frequency is noted, and the density of the test sample calculated using cell constants previously determined by measuring the oscillation frequencies when the cell is filled with calibration fluids of known density.

5 Apparatus

5.1 Density meter, capable, once calibrated, of determining density with a resolution of ± 0,1 kg/m^3 or better.

NOTES

3 Meters commonly display two forms of digital result, either a density value or the period of oscillation from which density can be calculated.

4 Research has shown that the density meter may show a bias of up to 1 kg/m^3 due to viscosity effects. Users should ascertain whether a viscosity correction is required by checking the result using a pyknometer method such as that given in ISO 3838. Alternatively, viscosity effects can be minimized by using certified calibration standards of chemical characteristics and viscosity similar to that of the sample under test [3].

5 Problems have been experienced with certain density meters due to condensation gathering on the cell sensors and electronics when the cell temperature is held below the dew-point of the ambient air. If there is risk of this occurring, the surrounding air should be kept dry.

5.2 Circulating constant-temperature bath, if required (see 9.1.2), capable of maintaining the temperature of the circulating liquid to within ± 0,05 °C of the required temperature.

5.3 Calibrated temperature sensor, capable of measuring the temperature of the cell to an accuracy of at least ± 0,10 °C.

The rate of energy transfer across the cell is low and therefore care should be taken to use sensors with very fine leads in order to minimize heat transfer in or out of the cell along the leads.

5.4 Homogenizer, suitable for the sample and sample container, and capable of producing homogeneous subsamples for test (see clause 8); a high speed shear or static mixer, or other type as appropriate.

6 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade.

6.1 Flushing solvent.

NOTE 6 Any solvent may be used provided that it is capable of producing a clean dry cell.

6.2 Ammonium peroxydisulfate, solution in concentrated sulfuric acid, 8 g/l.

WARNING — Ammonium peroxydisulfate is a strong oxidizing agent.

6.3 Calibration fluids.

A minimum of two calibration fluids are needed to calibrate the cell. They shall be chosen so that their densities bracket the density of the sample under test. The density of the calibration fluids shall be traceable to recognized national standards or based on internationally accepted values.

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[1] Institute of Petroleum, 61 New Cavendish Street, London W1M 8AR, UK.

[2] Bureau International des Poids et Mesures, Pavillon de Breteuil, F-92312 Sèvres Cedex, France.

When water and/or air are used, the requirements of 6.3.1 and 6.3.2 shall be met.

6.3.1 Water, conforming to ISO 3696 grade 2 or better.

Prior to use, pass the water through a 0,45 µm filter, and remove dissolved air by first boiling and then cooling. Once de-aired, handle the water carefully so as to minimize the amount of air redissolved.

Obtain the water density from the table given in Appendix G of IP *"Standard methods for analysis and testing of petroleum and related products"*. On publication of the BIPM tables (see clause 2), the values for density of water given therein shall be used.

NOTE 7 The density of water at various temperatures given in Appendix G has been prepared by the Institute of Petroleum, in order to provide a source for the density of water based on the International Temperature Scale 1990, whilst the work to produce new water-density tables, based on new water data, is carried out by BIPM[2)].

6.3.2 Air.

Use the values of the density of air given in Appendix H of IP *"Standard methods for analysis and testing of petroleum and related products"*. On publication of the BIPM tables (see clause 2), the values for density of ambient air given therein shall be used.

NOTE 8 The density of ambient air at various temperatures given in Appendix H has been prepared by the Institute of Petroleum, in order to provide a source for the density of ambient air based on the International Temperature Scale 1990, whilst work to produce new density of ambient air tables is carried out by BIPM.

6.4 Water, conforming to ISO 3696 Grade 3.

7 Sampling

Unless otherwise specified in a commodity specification, samples shall be taken as described in ISO 3170 or ISO 3171, and/or in accordance with the requirements of national standards or regulations.

Special care should be taken to prevent any loss of volatile components from the sample. Wherever possible samples should be drawn, transported and stored in the same container.

The sampling of volatile liquids using automatic techniques is not recommended unless a variable-volume sample receiver is used to collect and transport the sample to the laboratory. The use of a fixed-volume receiver (whether it is pressurized or not) could result in light-end loss from the material being sampled, thereby affecting the density measurement.

When drawing samples using variable-volume receivers, the sampling pressure and temperature of the sample source should be noted on the receiver label.

It is essential that the portion of the sample to be tested is representative of the bulk sample, and sample mixing is sometimes necessary to ensure homogenization prior to subsampling.

8 Sample preparation

8.1 General

Samples shall be handled in such a manner that:

a) light-end loss is minimized;

b) the temperature of the sample does not drop below:

   1) its cloud point, when determined in accordance with ISO 3015;

   2) or its wax appearance temperature (WAT), when determined in accordance with IP 389/93;

   3) or 20 °C above its pour point, when determined in accordance with ISO 3016.

NOTE 9 It should be recognized that loss of light ends during homogenization or heating, necessary when sediment, water or undissolved wax are present in samples of volatile crude petroleum or petroleum products, can cause errors in the determined density value.

8.2 Petroleum products which are free of water and/or sediments and which are sufficiently mobile

Mix by gentle shaking.

8.3 Crude petroleum and petroleum products containing water and/or sediments

Mix the sample in the original container, taking all precautions to minimize light-end loss.

NOTE 10 Mixing volatile crude petroleum and petroleum products in an open container will lead to loss of light components and is therefore not recommended.

8.4 Waxy crude petroleum

Warm the sample to 3 °C above the WAT or 20 °C above the pour point of the crude petroleum prior to mixing in the original container, taking all precautions to minimize light-end loss.

8.5 Waxy distillates

Warm the sample to 3 °C above the cloud point prior to mixing.

8.6 Fuel oils

Heat the sample until it is fluid prior to mixing.

9 Apparatus preparation

9.1 Test temperature

9.1.1 Sample density shall, wherever possible, be determined at the reference temperature.

If this is not possible, a temperature shall be chosen which is 3 °C above the cloud point or wax appearance temperature or 20 °C above the pour point and below the temperature at which gas appears in the sample.

9.1.2 If the density-meter cell is fitted with an integral thermostat, set the cell temperature according to the manufacturer's instructions. Otherwise, connect it to the constant-temperature bath (5.2). Allow the temperature to stabilize.

The manufacturer's specified working temperature and pressure ranges for the density-meter cell shall not be exceeded.

When temperature-controlled baths are used, ensure that the circulating liquid remains clean.

9.2 Cell cleaning

Clean and dry the cell using the flushing solvent (6.1) and if necessary water (6.4) followed by a water-miscible solvent (6.1) and blow dry with clean dry air.

After testing crude oils containing dissolved salts, clean the cell with water (6.4) after first washing with the flushing solvent (6.1).

If the cell shows signs of organic deposits, clean the cell by injecting ammonium peroxydisulfate solution (6.2) into the cell. After removal of the ammonium peroxydisulfate solution, flush the cell with water (6.4) followed by a water-miscible solvent (6.1) and blow dry with clean dry air.

10 Apparatus calibration

10.1 Density meters shall be calibrated when first installed, and whenever the test temperature is changed or when maintenance has been carried out or the system disturbed in any other way.

The density-meter calibration shall be verified within a period of not more than seven days prior to use.

10.2 Record the density reading or oscillating period with the clean cell filled with ambient air. If air is one of the calibrating fluids, omit 10.3.

10.3 Introduce the first calibration fluid (6.3) into the cell and allow the cell and its contents to reach temperature equilibrium. Record the oscillation period or the density reading and the temperature of the cell.

Clean the cell in accordance with the procedure given in 9.2.

10.4 Introduce the second calibration fluid into the cell and allow the cell and its contents to reach temperature equilibrium. Record the oscillation period or the density reading and the temperature of the cell.

10.5 Calculate the cell constants in accordance with the manufacturer's instructions.

10.6 After calibration, clean and dry the cell in accordance with the procedure given in 9.2.

11 Test procedure

11.1 Check that the density-meter reading when the cell is filled with ambient air is within ± 1 of the least significant digit compared to the reference value achieved during calibration (10.2). If it is not, reclean and dry the cell and repeat the check. If the reading still differs recalibrate the density meter.

11.2 Introduce the test portion of the sample into the cell using a suitable syringe or autosampler, filling the cell according to the manufacturer's instructions.

When testing waxy distillates or waxy crude oils or residual fuels oils, warm the syringe or autosampler to a temperature 3 °C above the cloud point or WAT, or 20 °C above the pour point of the material being tested.

11.3 When using an autosampler, either run samples in duplicate or introduce check samples, in order that errors due to bubble formation may be detected and the system performance monitored.

11.4 Do not apply suction to samples prone to light-end loss at any stage. Either the sample shall be poured into the syringe and then injected into the cell, or the autosampler shall be one which uses vial pressure to force the sample into the instrument.

11.5 When making a manual injection, switch on the cell illumination before injecting, check the cell for bubbles and fill in accordance with the manufacturer's instructions. If bubbles are detected, empty and refill the cell and recheck for bubbles.

Turn off the illumination immediately after examination of the cell, as heat generated by the light affects cell temperature.

11.6 When the density meter displays a reading steady to within 0,1 kg/m^3 for density, or to five significant figures for the oscillation period, note and record the indicated figure and the cell temperature to the nearest 0,1 °C.

NOTE 11 A consistent drift in the oscillation period or density reading normally indicates that the cell has not reached equilibrium temperature.

Random variations in readings normally indicate that air or gas bubbles are present in the cell. In this case, the cell should be recharged with a fresh sample. If the variations in reading are due to bubbles, it may be necessary to conduct the test at a lower temperature to ensure that the sample remains in a single phase.

If large water droplets are present in the sample due to inefficient mixing prior to sample introduction, the indicated density or oscillating period will tend to be erratic.

11.7 When measuring the density of viscous liquids, it is sometimes possible to obtain a stable reading even when gas or air bubbles are present. With these liquids, a slight overpressure shall be applied to the cell once the first density has been read, and the density redetermined. If the liquid is in single phase, the shift in density due to the additional pressure will be minimal. If, on the other hand, gas or air bubbles are present, a much larger shift in density will be observed as they are compressed. In such cases the cell shall be emptied and refilled with a fresh sample.

11.8 If the sample contains finely suspended water droplets, the density shall be observed as soon as thermal equilibrium has been reached.

NOTE 12 If samples containing finely suspended water droplets are left in the cell for a lengthy period, the water droplets will slowly coalesce and migrate to the cell antinodes, giving an apparent change in density.

11.9 Clean and dry the cell in accordance with the procedure given in 9.2.

12 Calculation

12.1 If the density meter displays an oscillation period, calculate sample density from the observed cell oscillation period in accordance with the manufacturer's instructions.

12.2 If the density is required at a reference temperature other than that at which it was determined, convert the density to the density at reference temperature using either ISO 91-1 for 15 °C or ISO 91-2 for 20 °C, after making an adjustment for the hydrometer correction (see annex A).

NOTE 13 ISO 91-1 and ISO 91-2 refer the user to the IP/ASTM/API Petroleum Measurement Tables and the IP Petroleum Measurement Paper Nos. 2 and 3.

13 Expression of results

Express the density to the nearest 0,1 kg/m^3, at the reference temperature.

14 Precision

14.1 Repeatability, r

The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, in the normal and correct operation of this test method, would exceed the values given below only in one case in 20.

Transparent middle distillates: $r = 0{,}2$ kg/m^3

Crude oils and other petroleum products: $r = 0{,}4$ kg/m^3

14.2 Reproducibility, R

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material, in the normal and correct operation of this test method, would exceed the values given only in one case in 20.

Transparent middle distillates: $R = 0{,}5$ kg/m^3

Crude oils and other petroleum products: R = 1,5 kg/m^3

NOTE 14 The precision was developed in accordance with ISO 4259.

15 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard (ISO 12185:1996);

b) the type and identification of the product under test;

c) the sampling procedures used (see clause 7);

d) the test temperature;

NOTE 15 When the test temperature is significantly different from the reference temperature, it is recommended that the observed density is also reported.

e) the result of the test (see clause 13);

f) any deviation, by agreement or otherwise, from the procedure specified;

g) the date of the test.

Annex A
(normative)

Hydrometer corrections to observed density

A.1 Background

Corrections to observed density are necessary when measured by methods other than by a soda-lime glass hydrometer or pyknometer calibrated at 15 °C before entry into IP 200, ASTM D 1250, API 2540, tables 53A, 53B or 53D.

The ISO 91-1 and ISO 91-2 standard implementation procedures include an option (switch) to allow for two types of density determination: those made using instruments with or without soda-lime glass. If parties mutually agree to use the printed tables instead of the standard, it shall be recognized that these tables are based on soda-lime glass instruments. If the printed tables 53A, 53B and 53D are entered with a density determined by any other method, it is necessary to first apply a correction to the observed value.

If it is agreed to use the printed tables, it is important to ensure that these are amended in accordance with the information provided in the IP document, *Petroleum Measurement Paper No. 2*.

A.2 Determination by a borosilicate glass hydrometer or pyknometer

If the density is determined by a hydrometer or pyknometer made of borosilicate glass, the observed value shall be adjusted for the difference between the expansion characteristics of the two types of glass as specified in ISO 3838.

A.3 Determination by a glass hydrometer calibrated at a temperature different from 15 °C

If density is determined by a glass (soda-lime or borosilicate) hydrometer or pyknometer calibrated at a temperature other than 15 °C, the observed value must be corrected as specified in ISO 3838:1983, subclause 10.3.4.5.

A.4 Determination by a device other than a glass hydrometer or pyknometer

If density is determined by a different type of device, not subject to the expansion of glass, an adjustment shall be made, before entering the printed tables 53A, 53B or 53D, cancelling the hydrometer correction incorporated in the table.

A.4.1 The corrections included in tables 53A, 53B and 53D were made by multiplying the observed density by the following factor:

$$1 - 0{,}000\,023(t - 15) - 0{,}000\,000\,02(t - 15)^2$$

where t is the temperature, in degrees Celsius.

To cancel this correction, the observed density is first multiplied by the reciprocal of this factor.

A.4.2 Example of correction cancellation applied to crude oil

Observed density = 875,5 kg/m^3 (not by glass hydrometer)

Observed temperature = 50 °C

To obtain the crude oil density at 15 °C:

a) calculate the glass correction factor as in A.4.1;

b) correct the density by multiplying the observed density by the reciprocal of the glass correction factor:

$$875{,}5 \times 1{,}000\,83 = 876{,}23 \text{ (rounded)}$$

c) enter the table with the corrected observed density at 50 °C and read off/calculate the density at 15 °C.