International Standard ISO 3838

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Crude petroleum and liquid or solid petroleum products — Determination of density or relative density — Capillary-stoppered pyknometer and graduated bicapillary pyknometer methods

Pétrole brut et produits pétroliers liquides ou solides — Détermination de la masse volumique ou de la densité relative — Méthodes du pycnomètre à bouchon capillaire et du pycnomètre bicapillaire gradué

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 3838 was developed by Technical Committee ISO/TC 28, *Petroleum products and lubricants*, and incorporates draft International Standard ISO/DIS 3658. Both documents were circulated to the member bodies in July 1981.

They have been approved by the member bodies of the following countries :

Australia	India	Romania
Austria	Iraq	South Africa, Rep. of
Belgium	Israel	Spain
Brazil	Italy	Sweden
Canada	Japan	Switzerland
China	Netherlands	United Kingdom
France	Norway	USA
Germany, F. R.	Peru *	USSR
Hungary	Poland	

No member body expressed disapproval of the documents.

* Peru approved DIS 3838 only.

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Crude petroleum and liquid or solid petroleum products — Determination of density or relative density — Capillary-stoppered pyknometer and graduated bicapillary pyknometer methods

1 Scope and field of application

1.1 This International Standard specifies methods for the determination of the density or relative density of crude petroleum and of petroleum products handled as liquids.

1.2 The capillary-stoppered pyknometer method is also for use with solids and this method may also be used for coal tar products, including road tars, creosote and tar pitches, or for mixtures of these with petroleum products. This method is not suitable for the determination of the density or relative density of highly volatile liquids having Reid vapour pressures greater than 50 kPa (0,5 bar) according to ISO 3007 or having an initial boiling point below 40 °C.

1.3 The graduated bicapillary pyknometer method is recommended for the accurate determination of the density or relative density of all except the more viscous products, and is particularly useful when only small amounts of samples are available. The method is restricted to liquids having Reid vapour pressures of 130 kPa (1,3 bar) or less according to ISO 3007 and having kinematic viscosities less than 50 cSt (50 mm^2/s) at the test temperature.

Special precautions are specified for the determination of the density or relative density of highly volatile liquids.

2 References

ISO 91, *Petroleum measurement tables.*[1)]

ISO 653, *Long solid-stem thermometers for precision use.*

ISO 3007, *Petroleum products — Determination of vapour pressure — Reid method.*

ISO 3507, *Pyknometers.*

ISO 5024, *Petroleum liquids and gases — Measurement — Standard reference conditions.*

3 Definitions

For the purpose of this International Standard, the following definitions shall apply.

3.1 density : The mass of the substance divided by its volume.

When reporting the density, the unit of density used, together with the temperature, shall be explicitly stated, for example kilograms per cubic metre, or grams per millilitre, at t °C.

3.2 apparent mass in air : The value obtained by weighing in air against standard masses without making correction for the effect of air buoyancy on either the standard masses or the object weighed.

3.3 observed density : The value required in order to enter tables 53A and 53B referred to in ISO 91/1 or given in table A in ISO/R 91 Addendum 1, determined with soda-lime glass apparatus at a test temperature which differs from the calibration temperature of the apparatus, no correction having been made for the thermal expansion or contraction of the glass.

3.4 relative density : The ratio of the mass of a volume of a substance at a temperature t_1 to the mass of an equal volume of another substance at a temperature t_2. The temperatures t_1 and t_2 may be equal. For the purpose of this International Standard, the other substance is water, i.e. the relative density is the ratio of the density of the substance at a temperature t_1 to the density of water at a temperature t_2.

When reporting the relative density, the temperatures t_1 and t_2 must be explicitly stated. ISO 91 refers only to tables for the reduction of relative density to 60/60 °F. If results are required referred to another reference temperature, the determination should be carried out at that temperature.

1) ISO 91/1 has been published, but the revision of ISO/R 91 Addendum 1 is at present at the stage of draft.

4 Principle

4.1 Capillary-stoppered pyknometer

The masses of equal volumes of the sample and of water are compared. Equal volumes are ensured by the pyknometer being filled so as to overflow when placed in a bath at the test temperature until equilibrium is reached. The calculation (clause 10) includes corrections for thermal expansion of glass and for buoyancy.

4.2 Graduated bicapillary pyknometer

The graduated arms of the pyknometer are calibrated, using water, in terms of the apparent mass in air of water contained in the pyknometer, and a graph prepared. The liquid sample is drawn into the dried pyknometer and, after it has reached equilibrium at the test temperature, the liquid levels are noted and the pyknometer weighed. The apparent mass in air of an equal volume of water is read from the graph and the density or relative density of the sample is calculated, with corrections being made as in 4.1.

5 Apparatus

5.1 Capillary-stoppered pyknometer, one of the three types shown in figure 1 (see 8.1.1).

The pyknometers shall conform to the relevant requirements of ISO 3507.

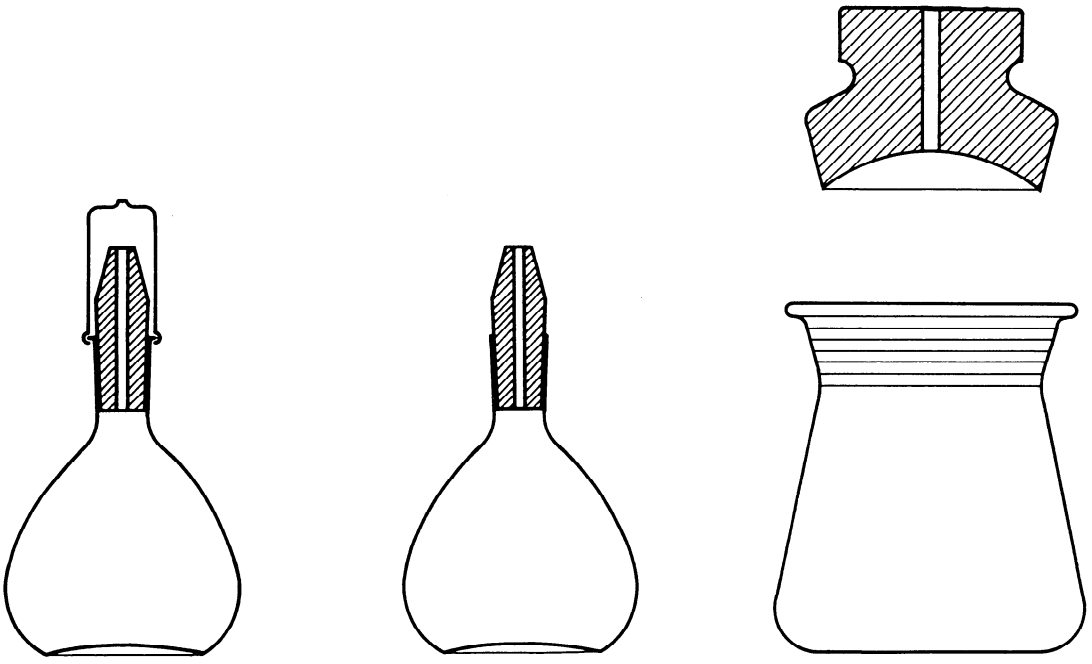
NOTE — The "warden" form [see a) in figure 1] is recommended for all except viscous or solid products and should always be used for volatile products. The ground glass cap, or "warden", greatly reduces expansion and evaporation losses and this form of pyknometer may be used when the test temperature is lower than that of the laboratory.

5.1.1 The form of pyknometer shown in b) in figure 1, known as the Gay-Lussac type, is suitable for non-volatile liquids except those of high viscosity.

5.1.2 The wide-mouth (Hubbard) form of pyknometer [see c) in figure 1] is used for very viscous liquids and solids.

5.1.3 As the forms of pyknometer shown in b) and c) in figure 1 have no "warden" or expansion chamber, they cannot be used when the temperature of the test is so far below that of the laboratory as to cause loss of sample by expansion through the capillary during weighing.

5.2 Graduated bicapillary pyknometer, capacity 1 to 10 ml, conforming to the dimensions given in figure 2, constructed of borosilicate glass or soda-lime glass, annealed after manufacture, and having a total mass not exceeding 30 g. Any pyknometer conforming with the requirements of the Lipkin pyknometer given in ISO 3507 may be used.



a) Warden pyknometer

b) Capillary-stoppered pyknometer

c) Wide-mouth capillary-stoppered pyknometer (Hubbard type)

Figure 1 — Capillary-stoppered pyknometers

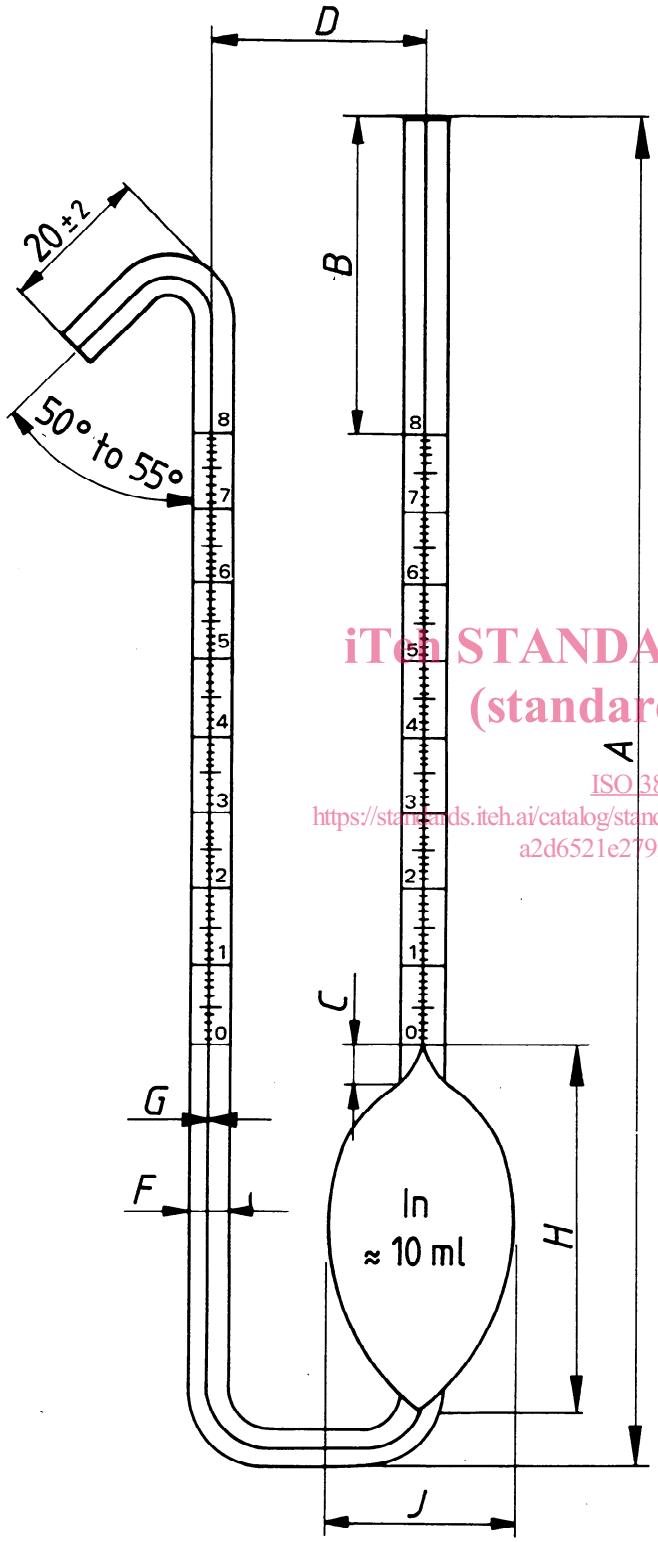


Figure 2 — Graduated bicapillary pyknometer (Lipkin type)

Table 1 — Characteristics of the graduated bicapillary pyknometer

Nominal capacity, ml	1	2	5	10
Difference between actual capacity and nominal capacity, max., ml	± 0,2	± 0,3	± 0,5	± 1
Maximum mass, g	30	30	30	30
Overall height, A, mm	175 ± 5			
Height above scale, B, min., mm	40			
Height from bulb to scale, C, min., mm	5			
Distance between centres of vertical limbs, D, mm	28 ± 2			
External diameter of tubing, F, mm	6			
Internal diameter of tubing, G, mm	1 ± 0,1			
Length from bottom of bulb to zero graduation line, H, mm	40			
External diameter of bulb, J, mm	11	14	20	25

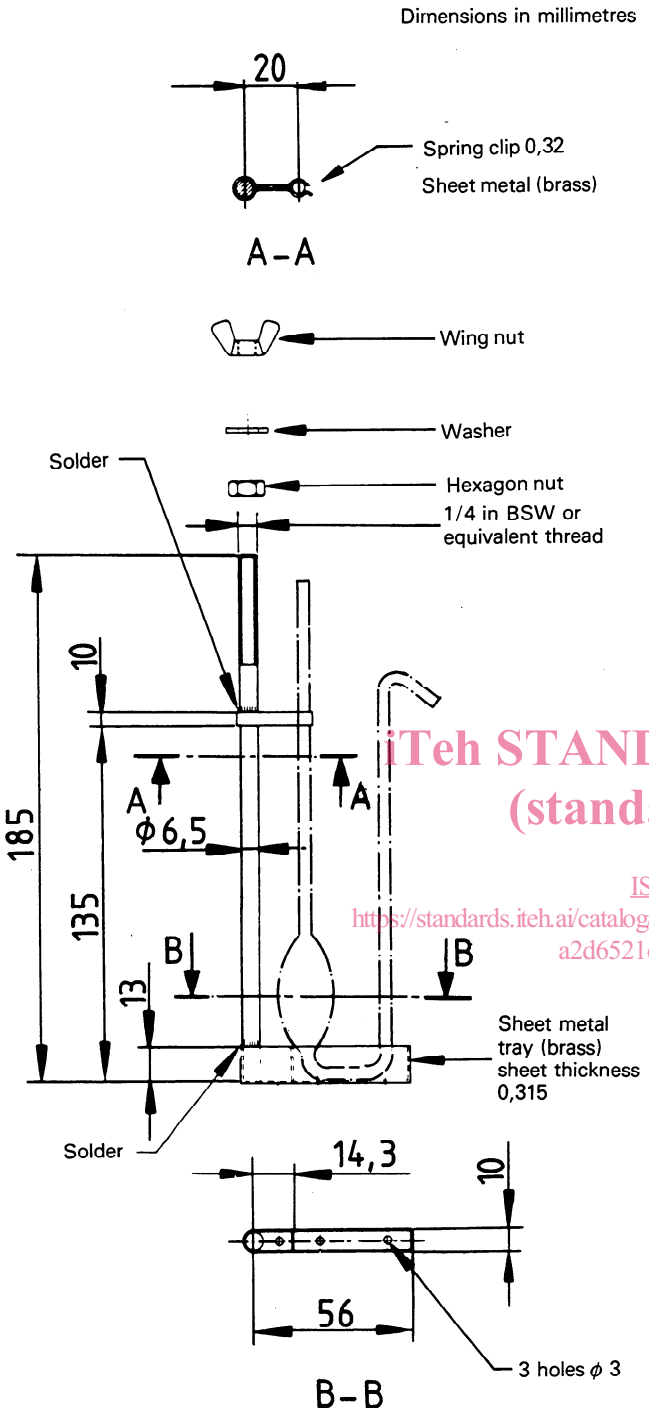


Figure 3 — A suitable design of holder for graduated bicapillary pyknometer

5.3 Constant-temperature water bath, having a depth greater than that of the pyknometer, capable of being maintained within 0,05 °C (0.1 °F) of the desired temperature.

5.4 Bath thermometer, conforming to the specification ISO 653/STL/0,1/−5/+ 25. Other total immersion thermometers of suitable range and equal or greater accuracy may also be used.

For the determinations of relative density 60/60 °F a Fahrenheit thermometer of suitable range graduated at 0.2 °F intervals may be used or the specified Celsius thermometer may be used at 15,56 °C.

5.5 Pyknometer holder (optional), to hold the pyknometer vertically and at the correct depth in the constant temperature bath. It shall be constructed of any suitable metal which will not corrode in the water bath.

A suitable design of holder for the graduated bicapillary pyknometers is shown in figure 3.

Several pyknometers holders may be conveniently supported in the water bath by the use of a non-corrodible rectangular metal bar of sufficient length to lie across the rim of the bath. A series of holes of sufficient diameter to accommodate the 6,5 mm rod of the pyknometer holder is drilled in the bar at about 45 mm apart. Each rod is secured in its hole by locking the bar between the hexagon nut, and the winged nut and washer.

5.6 Balance, capable of weighing to the nearest 0,1 mg.

6 Preparation of pyknometer

Thoroughly clean the pyknometer and stopper with surfactant cleaning fluid, rinse well with distilled water, then with a water-soluble volatile solvent such as acetone, and dry. Ensure that all traces of moisture are removed, using a current of filtered air if necessary. Cleaning should be carried out in this manner whenever the pyknometer is to be calibrated or whenever liquid fails to drain cleanly from the internal walls of the pyknometer or the capillary of the stopper. Normally the pyknometer may be cleaned between determinations by washing with a suitable light petroleum spirit such as 40/60 °C petroleum spirit, followed by vacuum drying.

NOTE — If surfactant cleaning fluids do not give adequate cleaning, chromic acid cleaning solution may be used. Chromic acid is a strong acid and powerful oxidizing agent and great care must be taken when using it.

7 Calibration of pyknometer

7.1 Conditioning

After drying, allow the pyknometer to reach room temperature. Dissipate any static charge which may have formed on it and then weigh to the nearest 0,1 mg.

NOTES

1 If the balance case is not fitted with a static eliminator, static charges may be dissipated by breathing on the pyknometer, but ensure that the pyknometer has regained constant mass before recording the mass.

2 For greatest accuracy, all the weighings should be made at temperatures within a 5 °C range so as to limit differences in air density.

7.2 Capillary-stoppered pyknometer

7.2.1 Fill the pyknometer with freshly boiled distilled water, cooled to slightly below the selected reference temperature, and firmly insert the stopper, taking care to avoid the inclusion of any air bubbles. Immerse the pyknometer to the neck in the constant-temperature bath and maintain it at 15 ± 0,05 °C, 20 ± 0,05 °C or 60 ± 0.1 °F as appropriate, for not less than 1 h.

7.2.2 When the pyknometer and its contents have reached the bath temperature, wipe the top of the stopper so that it is dry and the meniscus of the water in the capillary is flush with the top of the stopper. Care is necessary during this operation, since capillary action of the cloth can draw material out of the stopper. Place the "warden" firmly on the stopper (if the pyknometer is of this type).

7.2.3 Remove the pyknometer from the bath. If not of the "warden" form, cool the pyknometer and its contents to a temperature slightly below the temperature of the bath.

7.2.4 Dry the exterior surface of the pyknometer by wiping with a clean, lint-free cloth, dissipate any static charge and weigh to the nearest 0,1 mg.

7.2.5 The difference between the apparent masses in air of the filled and empty pyknometer gives the water equivalent at the selected reference temperature.

7.3 Graduated bicapillary pyknometer

7.3.1 Fill the pyknometer with sufficient freshly boiled, cooled, distilled water to obtain readings near the top of the graduated capillaries. Filling is readily achieved by placing the hooked tip in the liquid while keeping the pyknometer upright, thus allowing the liquid to be drawn over the bend in the capillary by capillary attraction. The pyknometer then fills by siphoning. Place the pyknometer in the constant-temperature bath so that the whole of the liquid in the pyknometer is below the level of the bath liquid. Maintain the temperature of the bath at 15 ± 0,05 °C, 20 ± 0,05 °C or 60 ± 0.1 °F, as required. Keep the pyknometer in the bath for 20 min then read the scale to the nearest small division at the liquid level in each arm.

7.3.2 Remove the pyknometer from the bath, allow the water on the exterior to drain off. The pyknometer may be dipped into acetone in a beaker to assist drying and wiped with a clean, dry, lint-free cloth. Allow it to come to room temperature, dissipate any static charge, and weigh to the nearest 0,1 mg.

7.3.3 The difference between the apparent masses in air of the filled and empty pyknometer gives the mass of water contained at the test temperature, corresponding to the sum of the two scale readings. By removing successive quantities of water, repeat the determination so as to obtain a series of at least three pairs of readings, together with the corresponding apparent masses in air, with the water level at different scale points on the graduated arms. One pair of readings shall be at the upper end of the scale and another at the lower end. Plot the sums of the scale readings on the two arms against the corresponding masses. The points should lie on a straight line which gives the mass of water contained by the pyknometer for any combination of scale readings. If the points show a scatter of more than two small scale divisions on either side of a straight line drawn through the array of points and subsequent tests do not correct this, discard the pyknometer as imperfect.

7.4 Other reference temperatures

If it is desired to determine the relative density referred to water at some temperature other than 60 °F or to determine density at a temperature other than 15 °C or 20 °C, calibrate the pyknometer at the desired temperature.

7.5 Recalibration

Recalibrate pyknometers at intervals as dictated by experience.

NOTE — It is recommended that new pyknometers should be recalibrated after one year, and thereafter at intervals dependent upon the magnitude of any changes found.

8 Procedure for capillary-stoppered pyknometers

8.1 Procedure for liquids

8.1.1 Choose an appropriate form and size of pyknometer for the sample to be tested. The 25 ml and 50 ml sizes are normally the most suitable.

8.1.2 Weigh the clean, dry calibrated pyknometer, if necessary dispersing any static charge (see notes following 7.1). Pyknometers of 25 ml or greater capacity should be weighed to the nearest 0,5 mg, and those of smaller capacity to the nearest 0,1 mg.

8.1.3 Fill the pyknometer with the test sample, if necessary warming both sample and pyknometer to assist filling and separation of air bubbles. Bring the pyknometer and its contents to the test temperature t_t (see 10.1) by immersing the pyknometer up to its neck in the constant-temperature bath (see note and 10.2.3). Immerse the pyknometer in the bath for 20 min in order to stabilize the temperature and to permit air bubbles to rise to the surface. If after this time the liquid level is still changing, keep the pyknometer in the bath until the liquid level becomes stable.

NOTE — For mixtures of products, it is essential to ensure that the test temperature is the same as the final reporting temperature unless an approximate value is acceptable and the volumetric composition of the mixture is known together with the correction coefficients of the components in the mixture.

8.1.4 When the temperature is constant, firmly insert the capillary stopper, which has also been brought to the test temperature, taking care to avoid trapping air bubbles below the stopper.

NOTE — It is essential to ensure that no air bubbles are left trapped in the liquid and adequate time must be allowed for air bubbles to rise to the surface before inserting the stopper.

Wipe excess liquid from the top of the stopper so that the meniscus of the liquid in the capillary is flush with the top of the stopper. Place the "warden" over the stopper (if the pyknometer is of this type).

8.1.5 Remove the pyknometer from the bath and, if not of the "warden" type, cool to a temperature slightly below t_t. Cool the pyknometer and contents to room temperature if the test temperature is above ambient.

8.1.6 Remove all traces of sample and water from the exterior surface of the pyknometer by wiping with a clean, lint-free cloth, disperse any static charge and weigh to the precision given in 8.1.2.

8.2 Procedure for solid or semi-solid samples

8.2.1 Weigh the clean, dry calibrated pyknometer, which should be of the wide-mouth type [see c) in figure 1], to the nearest 0,5 mg. For bituminous materials, only the wide-mouth type shall be used.

8.2.2 Introduce a suitable amount of the sample in the form of small pieces, which should be as regular as possible in order to reduce the possibility of trapping air bubbles. Alternatively, pour the molten sample into the warmed pyknometer, taking care to avoid the inclusion of air bubbles.

8.2.3 Bring the pyknometer and its contents to room temperature and weigh to the nearest 0,5 mg.

8.2.4 Fill the pyknometer with freshly boiled, cooled, distilled water, removing all air bubbles. A fine wire may be used to facilitate the removal of bubbles.

Bring the pyknometer and its contents to the test temperature t_t by immersing the pyknometer up to its neck in the constant-temperature bath. Immerse the pyknometer in the bath for 20 min in order to stabilize the temperature and to permit bubbles to rise to the surface. If after this time the liquid level is still changing, keep the pyknometer in the bath until the liquid level becomes stable.

8.2.5 When the temperature is constant, firmly insert the capillary stopper, which has also been brought to the test temperature, taking care to avoid trapping air bubbles below the stopper. Wipe excess water from the top of the stopper so that the meniscus of the water in the capillary is flush with the top of the stopper.

8.2.6 Remove the pyknometer from the bath and cool to a temperature slightly below t_t. Cool the pyknometer and contents to room temperature if the test temperature is above ambient.

8.2.7 Dry the exterior surface of the pyknometer by wiping with a clean, lint-free cloth, disperse any static charge and weigh to the nearest 0,5 mg.

9 Procedure for graduated bicapillary pyknometers

9.1 Weigh the clean, dry, calibrated pyknometer to the nearest 0,1 mg, dissipating any static charge if necessary. (See notes in 7.1.)

9.2 Fill the pyknometer with the sample at approximately the test temperature by the method specified in 7.3.1, so that the liquid levels are in the graduated portions of the capillaries (see note). If the test temperature is lower than the laboratory temperature, low scale readings should be aimed at in order to minimize any losses due to evaporation during weighing. Bring the pyknometer and contents to the test temperature t_t (see 10.1) by immersion for 20 min in the constant-temperature bath as specified in 7.3.1 and obtain readings of the liquid level in the two graduated arms. In the case of more viscous samples, no readings shall be taken until ample time for draining has been allowed after any disturbance of the pyknometer. The 20 min immersion time is normally sufficient, provided that the pyknometer has not been disturbed during this period.

NOTE — For mixtures of petroleum products and non-petroleum products it is essential to ensure that the test temperature is the same as the final reporting temperature, unless an approximate value is acceptable and the volumetric composition of the mixture is known together with the correction coefficients of the components in the mixture.

9.3 Remove the pyknometer from the bath, allow the water on the exterior to drain off. The pyknometer may be dipped into acetone in a beaker to assist drying and wiped with a clean, dry, lint-free cloth. Allow to come to room temperature, dissipate any static charge, and weigh to the nearest 0,1 mg.

9.4 When carrying out the determination on highly volatile samples containing appreciable amounts of material boiling below 20 °C, or on any sample where there is uncertainty concerning loss which might result from evaporation during the determination, cool the sample and pyknometer to a temperature of 0 to 5 °C before filling. If the dew point is sufficiently high to cause condensation of moisture in the pyknometer during the cooling operation, attach a drying tube to the arm of the pyknometer in order to avoid this. With samples of this type it is essential to restrict the filling of the pyknometer to obtain a low scale reading, thus minimizing losses due to evaporation. If the total length of unfilled capillary is over 10 cm, the rate of diffusion is so low that even with highly volatile compounds such as isopentane, vapour losses during the determination are negligibly low.

10 Calculation

10.1 Symbols

The following symbols are used in the calculations :

t_r is any reference temperature, e.g. 15 °C, ISO 5024 (see 10.2.1);

t_c is the temperature at which the pyknometer is calibrated by water filling, (see 10.2.2);

t_t is the temperature at which the pyknometer is filled with the liquid under test, (see 10.2.3);

m_o is the apparent mass in air, in grams, of the empty pyknometer;

m_c is the apparent mass in air, in grams, of the pyknometer filled with water at the calibration temperature t_c;

m_t is the apparent mass in air, in grams, of the pyknometer filled with the liquid under test at the temperature t_t;

m_1 is the apparent mass in air, in grams, of the pyknometer plus solid or semi-solid sample;

m_2 is the apparent mass in air, in grams, of the pyknometer plus sample, filled with water at the temperature t_t;

C is the correction for air buoyancy, in kilograms per cubic metre (see table 2) (see 7.1, note 2);

ϱ_c is the density of water, in kilograms per cubic metre, at the temperature of calibration t_c (see table 3);

α_1 is the coefficient of cubical expansion of borosilicate glass (see 10.3.2);

α_2 is the coefficient of cubical expansion of soda-lime glass (see 10.3.3);

ϱ_t is the density of the sample, in kilograms per cubic metre, at the test temperature t_t;

ϱ_r is the density of the sample, in kilograms per cubic metre, at any reference temperature t_r;

ϱ_{15} is the density of the sample, in kilograms per cubic metre, at the reference temperature of 15 °C;

ϱ_{20} is the density of the sample, in kilograms per cubic metre, at the reference temperature of 20 °C;

ϱ_t^1 is the observed density in kilograms per cubic metre at the test temperature t_t as determined in soda-lime glass apparatus calibrated at the reference temperature t_r = 15 °C or 20 °C, i.e. the observed density uncorrected for glass expansion required for entering the tables referred to in ISO 91.

NOTE — These calculations have been based on density in kilograms per cubic metre but if it is desired to use density in grams per millilitre the result should be divided by 1 000 (see clause 12).

d_t is the relative density at the test temperature t_t;

d_r is the relative density at the reference temperature t_r;

d_{60} is the relative density at the reference temperature of 60 °F;

d_t^1 is the observed relative density at the test temperature t_t as determined in soda-lime glass apparatus calibrated at the reference temperature t_r = 60 °F, i.e. the observed relative density uncorrected for glass expansion required for entering the tables referred to in ISO 91.

10.2 Reference, calibration and test temperatures

10.2.1 The standard reference temperature for international trade in petroleum and its products is 15 °C (ISO 5024), but other reference temperatures may be required for legal metrology or other special purposes.

10.2.2 The pyknometer may be calibrated at any convenient temperature and this may correspond with the reference, or test temperatures (see 7.1, note 2).

10.2.3 For qualitative purposes, the test temperature is usually chosen to correspond with the required reference temperature, but for quantitative purposes involving the calculation of the mass or of the apparent mass in air of a given quantity of oil, the density or relative density should be determined within 3 °C of the temperature at which the volume of oil is measured by the selected dynamic or static method. However, to minimize the loss of light fractions from very volatile samples, carry out the test at a temperature of 15 °C or below if the Reid vapour pressure exceeds the following :

a) for capillary-stoppered pyknometer — 10 kPa (0,1 bar),

b) for bicapillary pyknometer — 50 kPa (0,5 bar).

10.3 Correction for the thermal expansion of the pyknometer

10.3.1 General

The calculation of density or of relative density from measurements made at a temperature t_t which differs from the temperature t_c at which the pyknometer was calibrated, involves a correction for cubical expansion of the glass from which the pyknometer is made.

If the calculation is based on the density or relative density correction tables referred to, or given, in ISO 91, a similar correction may also be required (see 10.3.4).

10.3.2 Pyknometers made of borosilicate glass

10.3.2.1 The coefficients of cubical expansion of borosilicate glasses are known to depend on the source of the glass and to fall into three main categories having coefficients of cubical expansion of 10×10^{-6}, 14×10^{-6}, and 19×10^{-6} °C^{-1} respectively.

NOTE — In current production, pyknometers made of borosilicate glass usually have a coefficient of cubical expansion of 10×10^{-6} °C^{-1}.

10.3.2.2 For determination of the highest accuracy when borosilicate pyknometers are used therefore, either

a) ensure that $t_t = t_c$, or

b) use a pyknometer for which the coefficient of cubical expansion is known.