BRITISH STANDARD

BS 2000 :
Part 14 : 1994
ISO 4262 : 1993

Methods of test for

Petroleum and its products

Part 14. Petroleum products - Determination of carbon residue - Ramsbottom method

(Identical with IP 14/94)

British Standards

National foreword

This British Standard, having been prepared under the direction of the Petroleum Standards Policy Committee, was published under the authority of the Standards Board and comes into effect on 31 March 1994. It is identical with ISO 4262 : 1993, prepared by Technical Committee 28, Petroleum products and lubricants, of the International Organization for Standardization (ISO).

This British Standard supersedes BS 4451 : 1980, which is withdrawn.

BS 2000 comprises a series of test methods for petroleum and its products that are published by the Institute of Petroleum (IP) and have been accorded the status of a British Standard. Each method should be read in conjunction with the preliminary pages of 'IP Standard methods for analysis and testing of petroleum and related products' which gives details of the BSI/IP agreement for publication of the series, provides general information on safety precautions, sampling and other matters, and lists the methods published as Parts of BS 2000.

The numbering of the Parts of BS 2000 follows that of the corresponding methods published in 'IP Standard methods for analysis and testing of petroleum and related products'. Under the terms of the agreement between BSI and the Institute of Petroleum, BS 2000 : Part 14 will be published by the IP (in 'Standard methods for analysis and testing of petroleum and related products' and as a separate publication). BS 2000 : Part 14 : 1994 is thus identical with IP 14/94. Square brackets marked in the margin of this IP Standard indicate text that differs from the previous edition.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

The following BSI references
relate to the work of this
standard:
Committee reference PTC/13
Draft for comment 92/50648 DC

IP 14/94 ISO 4262:1993 ASTM D524-88 BS 2000 : Part 14 : 1994

Petroleum products — Determination of carbon residue — Ramsbottom method

1 Scope

This International Standard specifies a method for determining the amount of carbon residue, in the range of 0,01 % (*m/m*) to 30,0 % (*m/m*), left after evaporation and pyrolysis of an oil, and is intended to provide some indication of relative coke-forming tendency. The method is generally applicable to relatively non-volatile petroleum products which partially decompose on distillation at atmospheric pressure.

NOTES

1 The term "carbon residue" is used throughout this International Standard to designate the carbonaceous residue formed during evaporation and pyrolysis of a petroleum product. The residue is not entirely composed of carbon, but is a coke which can be further changed by pyrolysis. The term "carbon residue" is retained in this method only in deference to its widespread use.

2 The carbon residue of distillate and residual fuel oils gives an approximate ranking of such fuels in terms of their propensity to form deposits in specific applications.

3 The presence of alkyl nitrates in distillate fuels, or ash-forming additives in either distillate or residual fuels, will give carbon residue results that are higher than the corresponding values of the fuel without additives. These values may not correlate with the propensity of a fuel to form deposits.

4 The carbon residue of base lubricating oils may give an indication of the propensity of the oil to lay down deposits in combustion chambers, and/or of the relative chemical constitution of oils of similar viscosity. Most finished lubricating oils contain ash-forming additives, and thus the carbon residue of finished lubricants cannot be used in this manner.

5 The carbon residue of a gas oil is a useful guide in the manufacture of gas.

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 683-13:1986, *Heat-treatable steels, alloy steels and free-cutting steels — Part 13: Wrought stainless steels.*

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

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

ISO 3405:1988, *Petroleum products — Determination of distillation characteristics.*

3 Principle

3.1 The test portion is weighed into a glass coking bulb having a capillary opening, and is placed in a metal furnace maintained at a temperature of approximately 550 °C. The test portion is thus quickly heated to the point at which all volatile matter is evaporated out of the bulb with or without decomposition, while the heavier residue remaining in the bulb undergoes cracking and coking reactions. In the later stages of the heating period, the coke or carbon residue is subject to further slow decomposition or slight oxidation due to the possibility of air being drawn into the bulb. After a specified heating period, the bulb is removed from the furnace, cooled in a dessicator, and again weighed. The residue remaining is calculated as a mass percentage of the test portion.

3.2 Provision is made for determining the proper operating characteristics of the furnace with a control bulb containing a thermocouple, which gives a specified time-temperature relationship.

3.3 For light products where over 90 % (*V/V*) distils at below 370 °C, the procedure may be carried out on the residue remaining after 90 % (*V/V*) has been distilled. The procedure for obtaining this residue is given in annex A.

4 Apparatus

4.1 Glass coking bulb, made of heat-resistant glass, and conforming to the dimensions and tolerances shown in figure 1.

Prior to use, check the diameter of the capillary to see that it is greater than 1,5 mm and not more than 2,0 mm. Pass a 1,5 mm diameter drill rod through the capillary and into the bulb; attempt to pass a 2,0 mm diameter drill rod through the capillary. Reject bulbs that do not permit the insertion of the smaller rod and those whose capillaries are larger than the larger rod.

4.2 Control bulb, for use in determining compliance of furnace characteristics with the performance requirements (see clause 5). Made of stainless steel, containing a thermocouple and conforming to the tolerances shown in figure 2. The control bulb shall be provided with a dull finish by heating in a furnace at a temperature of 850 °C to 900 °C for 30 min, and shall not be polished thereafter, as a polished bulb has different heating characteristics from one with a dull finish.

A suitable thermocouple pyrometer for observing true temperature within ± 1 °C is also required.

4.3 Syringe, for test portion charging. A 5 ml or 10 ml glass hypodermic syringe fitted with a needle of 1,5 mm outside diameter or a serum needle of 1,45 mm to 1,47 mm outside diameter, for transfer of the test portion to the glass coking bulb.

NOTE 6 A syringe having a needle which fits on the ground glass tip of the syringe is not recommended, as it may be blown off when pressure is applied to the syringe plunger. Locking-type syringes are more satisfactory, as the needle locks on the bottom of the syringe barrel, and cannot be blown off by pressure.

4.4 Metal coking furnace, constructed of solid metal, having coking bulb wells 25,45 mm ± 0,1 mm in internal diameter and 76 mm deep to the centre of the well bottom, with suitable arrangements for heating to a uniform temperature of 550 °C. The bottom of the well shall be hemispherical to accommodate the bottom of the glass coking bulb (4.1).

Do not cast or otherwise form the furnace with unnecessary voids which will impede heat transfer.

If a molten metal furnace is used, provide it with a suitable number of bulb wells, the internal dimensions of which correspond to the internal dimensions of holes in the solid metal furnace. The bulb wells shall be immersed in the molten metal to leave not more than 3 mm of the bulb well exposed above the molten metal at operating temperatures.

Dimensions in millimetres

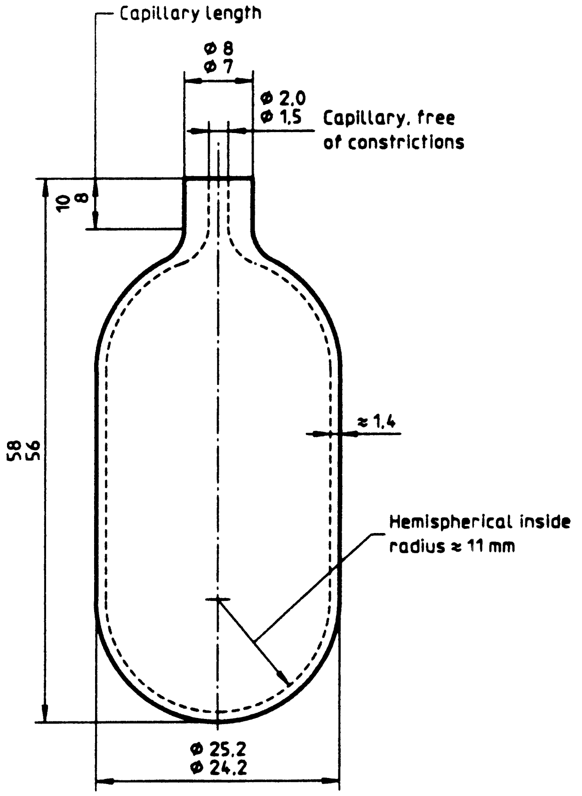


Figure 1 — Glass coking bulb

NOTE 7 A description of one type of furnace which has been found to be satisfactory is given in annex B.

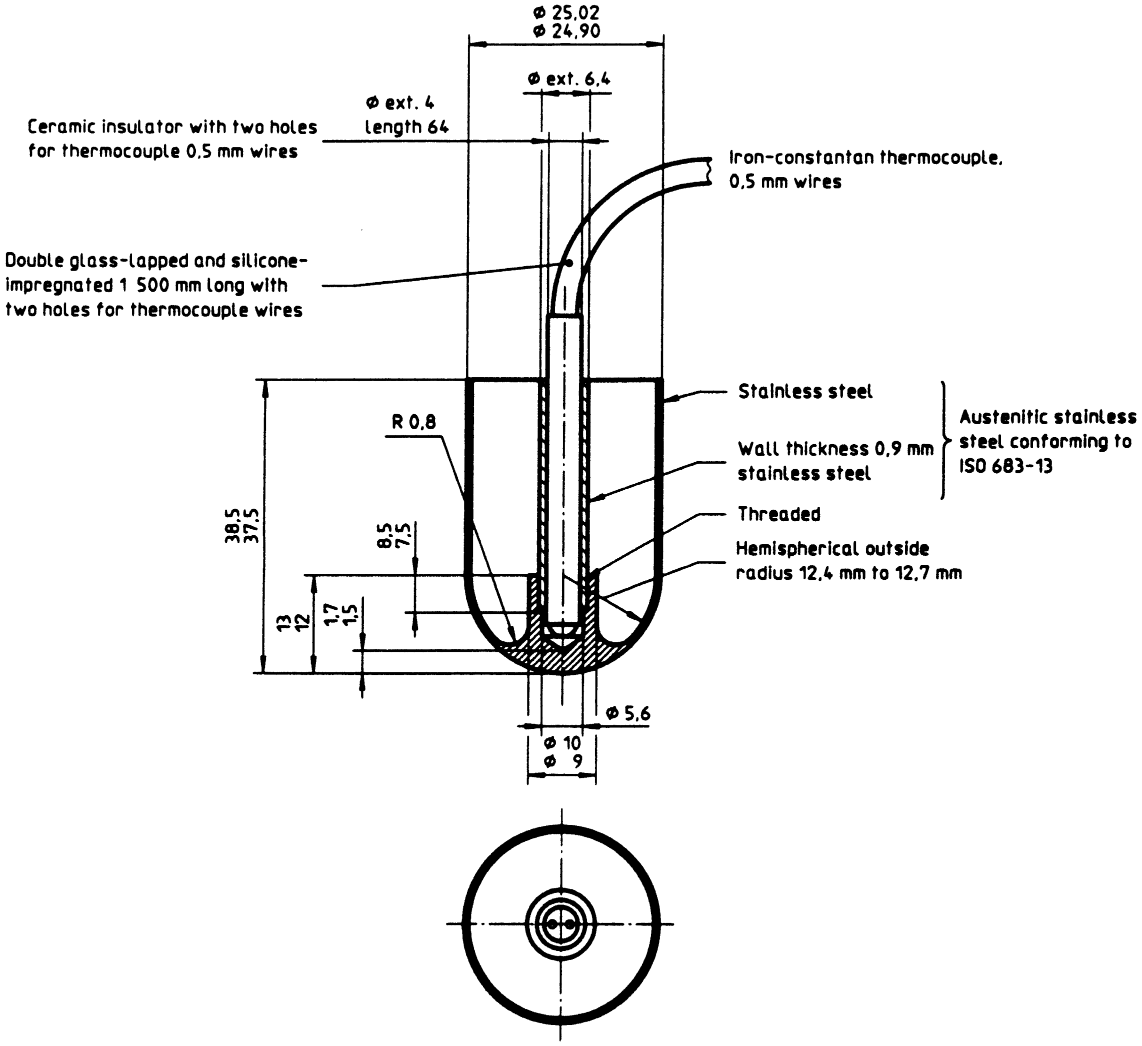
4.5 Temperature-measuring devices. A removable iron-constantan thermocouple with a sensitive pyrometer, or other suitable temperature-indicating device shall be used, located centrally near the bottom portion of the furnace and arranged to measure the temperature of the furnace, thus enabling the performance tests specified in clause 5 to be carried out.

NOTES

8 When a molten bath is used, it is desirable to protect the temperature-indicating device with a quartz or thin metal sheath.

9 It is good practice to calibrate the thermocouple or other temperature-measuring device against a standard thermocouple or a reference standard approximately once a week when the furnace is in constant use, the actual frequency depending on experience.

Dimensions in millimetres
Tolerance on dimensions ± 0,4 unless otherwise stated



NOTE — Total mass of control bulb less thermocouple: 24 g ± 1 g

Figure 2 — Control bulb

5 Verification of apparatus performance

5.1 General

Periodically check the performance of the furnace (4.4) and temperature-measuring devices (4.5) as described in 5.2 to 5.4 to ensure that as used they conform to the requirements of the method. Consider the furnace as having standard performance when the operating requirements described are met by each coking bulb well while the bath is fully loaded as well as singly loaded. Once these criteria have been met, use the furnace with any degree of loading. Use only a furnace that has successfully undergone the performance or control tests given in this clause.

5.2 Thermocouple

Calibrate the thermocouple in the control bulb against a standard thermocouple at least once every 50 h of use of the control bulb (4.2).

NOTE 10 During use at the high temperature of the test, iron-constantan thermocouples oxidize and their calibration curves change.

5.3 Fully-loaded furnace

When the furnace temperature is within a previously chosen 2 °C temperature range within the general range 550 °C ± 5 °C (which is to be used thereafter with that particular furnace for both standardization and routine operation), insert the control bulb (4.2) in one well. Within 15 s, insert in each of the other wells a glass coking bulb (4.1) containing 4 g ± 0,1 g of a viscous neutral petroleum lubricating oil with a viscosity within the range 60 mm^2/s to 100 mm^2/s at 40 °C. With a suitable accurate potentiometer or millivoltmeter (sensitive to 1 °C or less), observe the temperature rise in the control bulb at 1 min intervals for 20 min. If the temperature in the control bulb reaches 547 °C in not less than 4 min and not more than 6 min from the instant of its insertion in the furnace, and remains within the range 550 °C ± 3 °C for the remaining portion of the 20 min test, consider that particular coking bulb well to be suitable for use as a "standard performance well" when the furnace is used fully loaded. Check each well in a similar fashion, with the furnace fully loaded each time.

5.4 Singly-loaded furnace

When the furnace temperature is within a previously chosen 2 °C temperature range within the general range 550 °C ± 5 °C (which is to be used thereafter with that particular furnace for both standardization and routine operation), insert the control bulb (4.2) in one well, with the remaining wells unoccupied. With a suitable accurate potentiometer or millivoltmeter (accurate to 1 °C or less), observe the temperature rise in the control bulb at 1 min intervals for 20 min. If the temperature in the control bulb reaches 547 °C in not less than 4 min and not more than 6 min from the instant of its insertion in the furnace, and remains within the range 550 °C ± 3 °C for the remaining portion of the 20 min test, consider that particular coking bulb well to be suitable for use as a "standard performance well" when the furnace is used with only a single bulb. Check each well in a similar fashion, with the furnace singly loaded each time.

It is possible that not all of the wells in old furnaces will meet the requirements when fully loaded and singly loaded, and if this is the case, check each well for any degree of furnace loading which may be used. For example, if not more than three wells of a six-well furnace are used at any one time, choose the three wells to be used from the performance data obtained with fully-loaded and singly-loaded furnaces. Check each of the three wells for triple loading, two of the wells for double loading, and one for single loading. Use the checked wells and no others in applying the test procedure.

6 Samples and sampling

6.1 Obtain samples in accordance with ISO 3170, ISO 3171 or an equivalent national standard.

6.2 Products examined by this International Standard are not always completely homogeneous, and therefore appropriate precautions shall be taken during the procurement of both bulk and laboratory test samples (see 7.2).

7 Test procedure

7.1 Place a new glass coking bulb (4.1) (see note 11) in the coking furnace (4.4) at 550 °C for approximately 20 min to decompose any foreign organic matter and to remove water. Do not re-use a glass coking bulb, as unpredictable results can be obtained in such cases. Place the bulb in a closed desiccator over calcium chloride or silica gel for 20 min to 30 min and then weigh to the nearest 0,1 mg.

NOTE 11 For routine testing, new bulbs may be used without pre-ignition provided that they are visibly free from particles or other contamination.

7.2 Shake thoroughly the oil sample to be tested, first warming if necessary to reduce its viscosity. Strain the sample through a 150 µm wire sieve. By means of the hypodermic syringe (4.3) or the device shown in figure 3, introduce into the coking bulb an amount of sample as indicated in table 1. Ensure that no oil remains on the exterior surface or on the inside of the neck of the bulb. Reweigh the bulb and contents to the nearest 0,1 mg.

Table 1 — Test portion mass

Ramsbottom carbon residue % *(m/m)*	**Test portion mass** g
< 6,00	4,0 ± 0,1
6,00 to 14,0	1,0 ± 0,1
14,1 to 30,0	0,5 ± 0,1

NOTES

12 If difficulty is encountered in loading very viscous or asphaltic test portions, of whatever size, into the glass coking bulb, the apparatus shown in annex B may be used.

13 When obtaining the test portion of oils containing sediment (for example, used oils), it is important to make the transfer of test portions in the shortest possible time to avoid segregation of the sediment. Samples containing sediment which settles quickly after stirring can be placed in the coking bulbs more expeditiously by using an arrangement such as that shown in figure 3. This device consists of a three-way 2 mm stopcock to which have been fused two lengths of capillary tubing (1,5 mm to 2,0 mm

internal diameter). Connect the third leg of the stopcock to a vacuum line by means of pressure tubing.

Secure the glass coking bulb to the short arm of capillary tubing by a 25 mm length of hose, taking care that the capillary of the glass bulb is butted up against the capillary tubing. Immerse the long end of the capillary tubing in the sample. After evacuating the coking bulb, manipulate the stopcock to cause the stirred sample to flow freely into the bulb through the two lengths of capillary tubing. Use tubing with the same internal diameter as that of the neck of the coking bulb to prevent accumulation of any sediment during transfer.

7.3 Place the coking bulb in a "standard performance well" with the furnace at the checking temperature (see note 14) and allow to remain for 20 min ± 2 min. Remove the bulb with metal tongs, the tips of which have just been heated. Reproduce the furnace and bulb condition used when standardizing that bulb well (5.1, 5.3 and 5.4). If there is appreciable loss of oil from frothing, discard the test and repeat the determination using a smaller test portion (see note 15).

NOTES

14 When carrying out a test, it is important to adhere rigorously to the temperature conditions chosen for checking performance of apparatus (see clause 5); for example, if the bath was at a temperature of 553 °C ± 1 °C when inserting the control bulb (4.2), then it is necessary to use similar temperature conditions in the coking test. When maintained in normal operation, the temperature of an electrically heated furnace with automatic controls will generally fluctuate within a specific temperature range. Therefore, when making a coking test, it is generally important that the test bulbs be inserted when the furnace is at the same temperature and at the same position in the temperature cycle as it was when the inspection test was started, unless it has been proved that the temperature variations are insignificant.

15 Frothing may be due to water which can be removed by heating gently in a vacuum and flushing out the vapour with nitrogen prior to filling the bulb.

7.4 After removal, cool the bulb in a desiccator under the same conditions (including time for weighing) used before filling the bulb (see 7.1). When removing the bulb from the desiccator, examine to make sure there are no foreign particles adhering to the bulbs; if any are found, as black particles sometimes are on the capillary neck, brush them off with a piece of sized paper or a camel hair brush. Weigh to the nearest 0,1 mg. Discard the used glass coking bulb.

NOTE 16 In studies of oil characteristics, useful information can often be obtained from a simple visual examination of the coking bulb after the test. Thus, significance can be attached to noting, in the results, such findings as whether coke more or less fills the bulb; whether liquid material is present, either as limpid residue or drops; whether the residue is not black and flaky, but is coloured and powdery (presumably from the presence of inorganic material).

Dimensions in millimetres

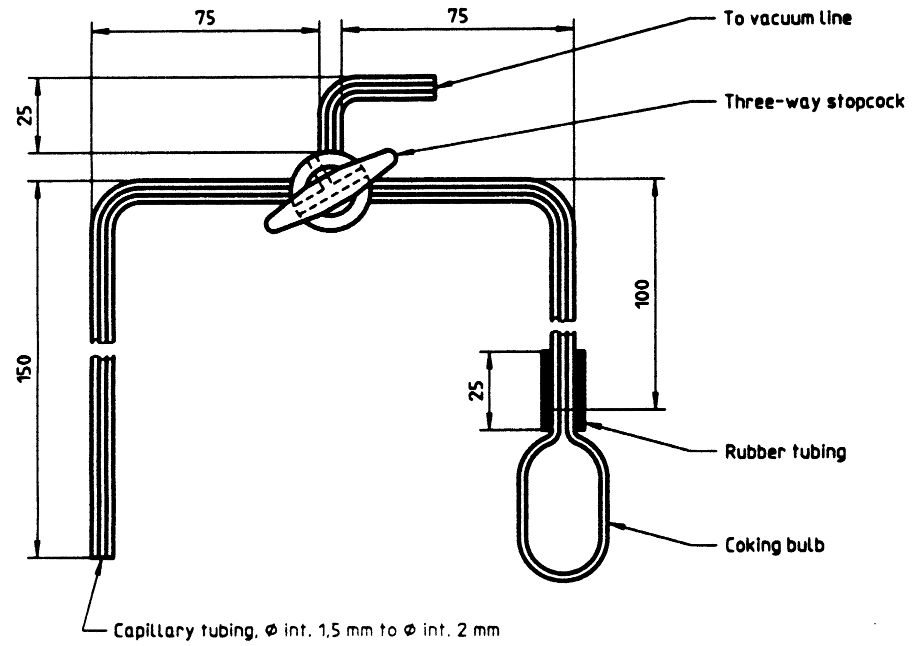


Figure 3 — Sampling device

8 Calculation

Calculate the carbon residue of the sample, or of the 10 % (*V/V*) distillation residue (10 % b), using equation (1):

$$\text{Carbon residue, \% } (m/m) = \frac{m_3 - m_1}{m_2 - m_1} \times 100 \quad \ldots (1)$$

where

m_1 is the mass of empty coking bulb, in grams;

m_2 is the mass of coking bulb + test portion, in grams;

m_3 is the mass of coking bulb + residue, in grams.

9 Expression of results

9.1 Report results obtained from equation (1) as "Carbon residue — Ramsbottom", or "Carbon residue — Ramsbottom (10 % b)" with a reference to this International Standard.

9.2 Express the results to the nearest 0,01 % (*m/m*) up to 9,99 % (*m/m*), and to the nearest 0,1 % (*m/m*) from 10,0 % (*m/m*) to 30,0 % (*m/m*).

10 Precision

10.1 The precision is shown graphically in figure 4.

10.2 The repeatability (*r*), or 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 value below only in one case in 20:

$$\lg r = -1{,}069\,40 + 0{,}752\,38 \lg x + 0{,}236\,82 (\lg x)^2$$

where x is the average of the results being compared, in % (*m/m*).

10.3 The reproducibility (*R*), or the difference between two single and independent results, obtained by different operators working in different laboratories on nominally identical test material, would in the long run, in the normal and correct operation of the test method, exceed the value below only in one case in 20:

$$\lg R = -0{,}853\,33 + 0{,}789\,07 \lg x + 0{,}190\,14 (\lg x)^2$$

where x is the average of the results being compared, in % (*m/m*).

11 Test report

The test report shall contain at least the following information:

a) the type and complete identification of the product tested;

b) a reference to this International Standard;

c) the results of the test (see clause 9);

d) any deviation, by agreement or otherwise, from the standard procedures specified;

e) the date of the test.

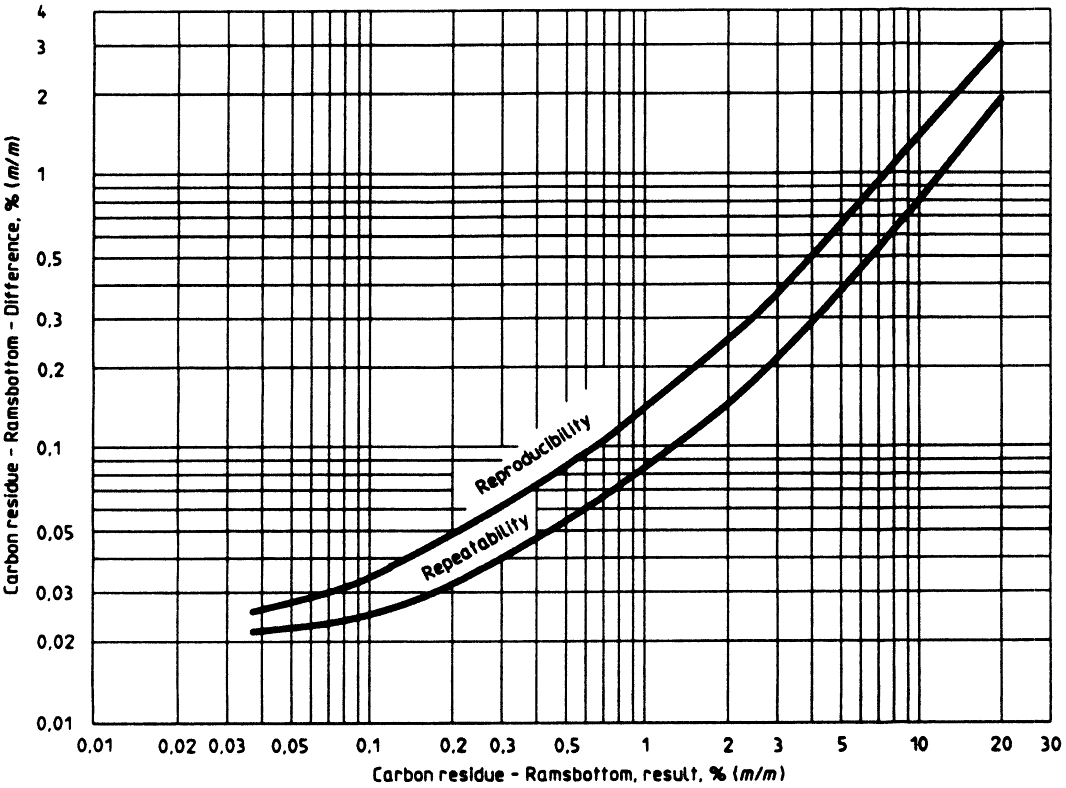


Figure 4 — Precision data

Annex A
(normative)

Procedure for the preparation of a 10 % (*V/V*) distillation residue

A.1 Apparatus

A.1.1 Distillation flask, 250 ml, of borosilicate glass, conforming to the dimensions shown in figure A.1.

A.1.2 Cylinder, 200 ml, graduated, and conforming to the dimensions shown in figure A.2.

A.1.3 Distillation apparatus, conforming to that described in ISO 3405 with the exceptions of A.1.1 and A.1.2.

NOTE 17 A thermometer is not essential, but the use of the high temperature range thermometer described in ISO 3405 is recommended.

A.2 Test procedure

A.2.1 Place a volume of sample equivalent to 200 ml ± 1 ml at 13 °C to 18 °C in the flask. Either maintain the temperature of the cooling bath at 0 °C to 4 °C or, if the distillate is known to be waxy (and therefore may solidify in the condenser tube), raise the cooling bath temperature during the distillation to a temperature that maintains condensation but allows the distillate to flow. The maximum temperature of the cooling bath shall be 60 °C. Use, without cleaning, the cylinder from which the sample was measured as the receiver and place it so that the tip of the condenser does not touch the wall of the cylinder. Insert a snug-fitting cork, with or without a thermometer (see A.1.3), into the neck of the flask.

A.2.2 Apply heat to the flask at a uniform rate so regulated that the first drop of condensate falls from the condenser 10 min to 15 min after initial application of heat. After the first drop falls, move the measuring cylinder so that the tip of the condenser tube touches the wall of the cylinder. Then regulate the heat so that the distillation proceeds at a uniform rate of 8 ml to 10 ml per min. Continue the distillation until 178 ml ± 1 ml of distillate has been collected, then discontinue heating and allow the condenser to drain until 180 ml (90 % of the charge in the flask) has been collected in the cylinder.

A.2.3 Immediately replace the cylinder with a small flask and catch any final drainage in the flask. Add to this flask the still-warm residue left in the distilling flask, and mix well. The contents of the flask then represents a 10 % distillation residue from the original product (assuming no volatile loss).

A.2.4 While the distillation residue is warm enough to flow freely, place 4,0 g ± 0,1 g of it into the previously weighed coking bulb (4.1).

NOTE 18 The hypodermic syringe (4.3) provides a convenient means of performing this operation.

After cooling, weigh the bulb and contents to the nearest 0,1 mg and follow the procedure in 7.3 and 7.4 of this International Standard.

Dimensions in millimetres

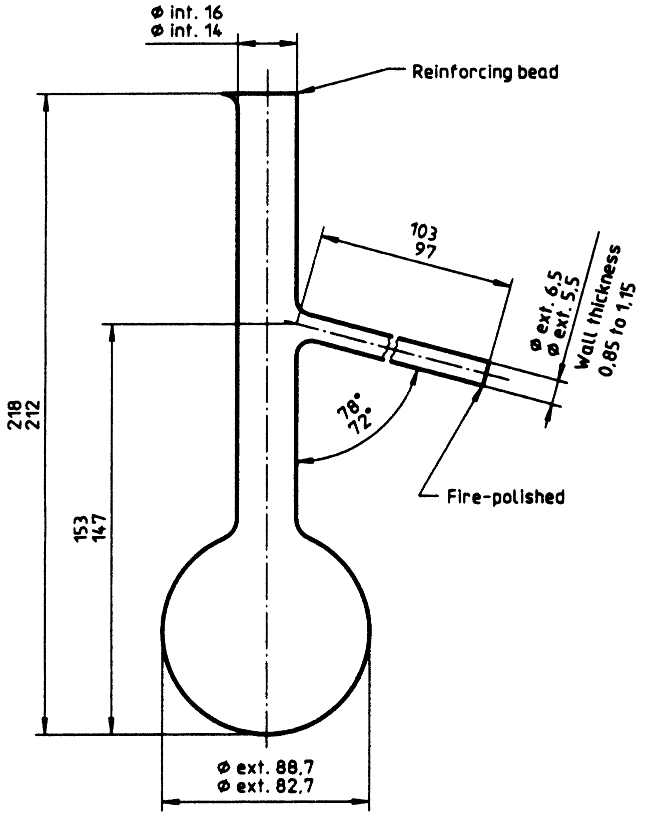
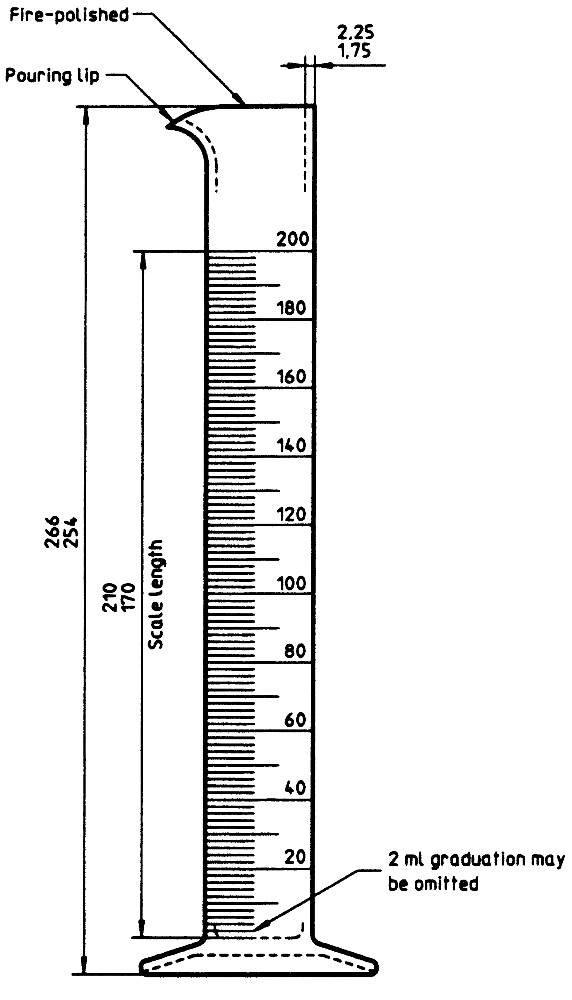


Figure A.1 — 250 ml distillation flask

Dimensions in millimetres



Shape of foot optional;
cylinder must stand on 15°
slope without tipping

Figure A.2 — 200 ml measuring cylinder

Annex B
(informative)

Examples of suitable apparatus

B.1 Solid metal furnace

The major difficulty in achieving satisfactory precision for the Ramsbottom method is the need for a uniformly operating furnace. The type of solid metal furnace illustrated in figure B.1 meets the performance characteristics specified in clause 5 of this International Standard. It may be constructed of cast iron or other suitable metal for use under the high temperature conditions which are employed in this method of test. It is desirable to cast the metal without any unnecessary voids. Use of a substantial mass of metal for the block avoids the requirement for an excessive amount of electrical heating which could cause wide fluctuations in block temperature unless very sensitive controls were used.

B.2 Coking bulb filling device

When samples too viscous to handle at room temperature are to be tested, the coking bulb can be filled from a vertically-mounted 5 ml or 10 ml syringe using a spring to activate the plunger. The glass coking bulb filling device shown in figure B.2 has been found satisfactory for this purpose. The illustrated stand is made of 3 mm brass plate and can be modified to hold any number of syringes of either the 5 ml or 10 ml type. For convenience, a number of syringes can be permanently mounted in the stand.

To use the coking bulb filling device, warm the oil sample to be tested until it is fluid. Place a coking bulb in position under the syringe and remove the plunger of the syringe from the barrel. Pour a representative portion of the sample into the barrel of the syringe, lubricate the plunger with one or two drops of white oil and replace in the barrel. Then place the loaded syringe in the rack as shown, with the spring-loaded clip fitted over the plunger head and with the tip of the needle extending into the bulb. Place the entire assembly in an oven maintained at the lowest temperature that will permit the sample to flow sufficiently to load the bulb. As soon as a sufficient test portion has been forced into the coking bulb, remove and weigh the bulb and its contents and proceed as described in 7.3. Remove the assembled apparatus from the oven as soon as possible, as extended heating periods may alter the carbon residue value of the sample.

Dimensions in millimetres

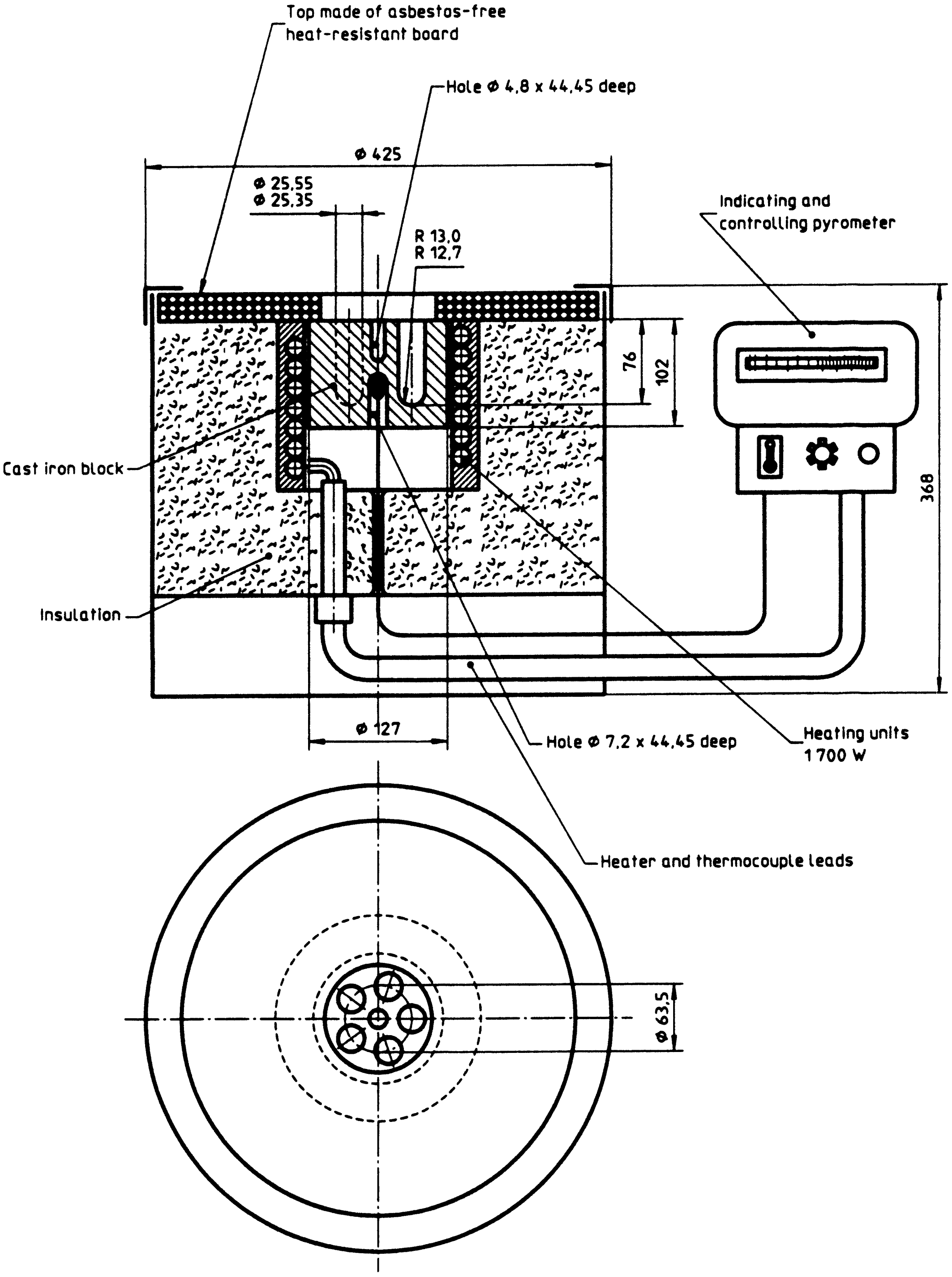


Figure B.1 — Solid metal furnace

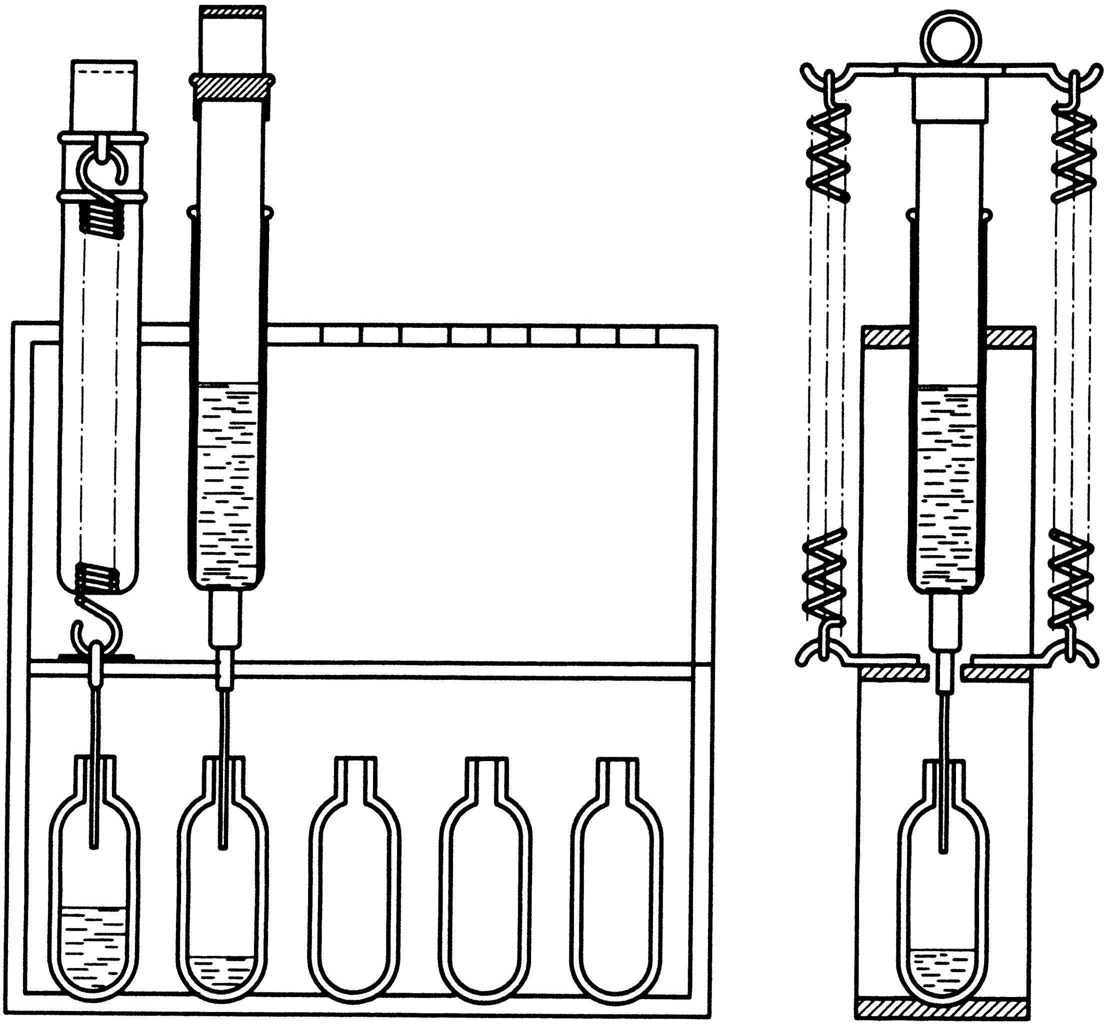


Figure B.2 — Coking bulb filling device

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