

INTERNATIONAL STANDARD



4262

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Petroleum products — Determination of carbon residue — Ramsbottom method

Produits pétroliers — Détermination du carbone résiduel — Méthode «Ramsbottom»

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FOREWORD

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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 4262 was developed by Technical Committee ISO/TC 28, *Petroleum products*, and was circulated to the member bodies in May 1976.

It has been approved by the member bodies of the following countries :

Australia	India	Portugal
Austria	Iran	Romania
Belgium	Ireland	South Africa, Rep. of
Brazil	Israel	Spain
Canada	Italy	Sweden
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No member body expressed disapproval of the document.

Petroleum products — Determination of carbon residue — Ramsbottom method

1 SCOPE AND FIELD OF APPLICATION

1.1 This International Standard specifies a method for determining the amount of carbon residue (see note) 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.

NOTE — The term "carbon residue" is used throughout this method 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.

1.2 The carbon residue value of burner fuel serves as a rough approximation of the tendency of the fuel to form deposits in vaporizing pot-type or sleeve-type burners. The carbon residue value of gas oil is useful as a guide in the manufacture of gas from gas oil, while carbon residue values of crude oil residues, cylinder oils and bright stocks, are useful in the manufacture of lubricants.

1.3 The following anomalous cases should be noted :

- a) *Motor oils.* The carbon residue value of motor oil, while at one time regarded as indicative of the amount of carbonaceous deposits a motor oil would form in the combustion chamber of an engine, is now considered to be of doubtful significance due to the presence of additives in many oils. For example, an ash-forming detergent additive may increase the carbon residue value of an oil yet will generally reduce its tendency to form deposits.
- b) *Diesel fuels.* The carbon residue value of diesel oils containing amyl nitrate is erroneously high. If, however, the test is carried out on diesel fuels not containing amyl nitrate or on the base fuel to be blended with amyl nitrate, the carbon residue value correlates approximately with combustion chamber deposits.
- c) *Petroleum products containing ash-forming additives* may give carbon residue values which may not correlate with the tendency to form deposits and may be higher than the corresponding tendency to form deposits.

2 REFERENCE

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

3 PRINCIPLE

3.1 The test portion, after being weighed into a glass coking bulb having a capillary opening, 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 desiccator, and again weighed. The residue remaining is calculated as a percentage of the test portion, and reported as Ramsbottom carbon residue.

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

3.3 If a product has a Ramsbottom carbon residue of less than 0,1 %, the procedure is modified by carrying out the test on a 10 % distillation residue.

4 APPARATUS

4.1 **Glass coking bulb**, of heat-resistant glass, 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 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.

Dimensions in millimetres

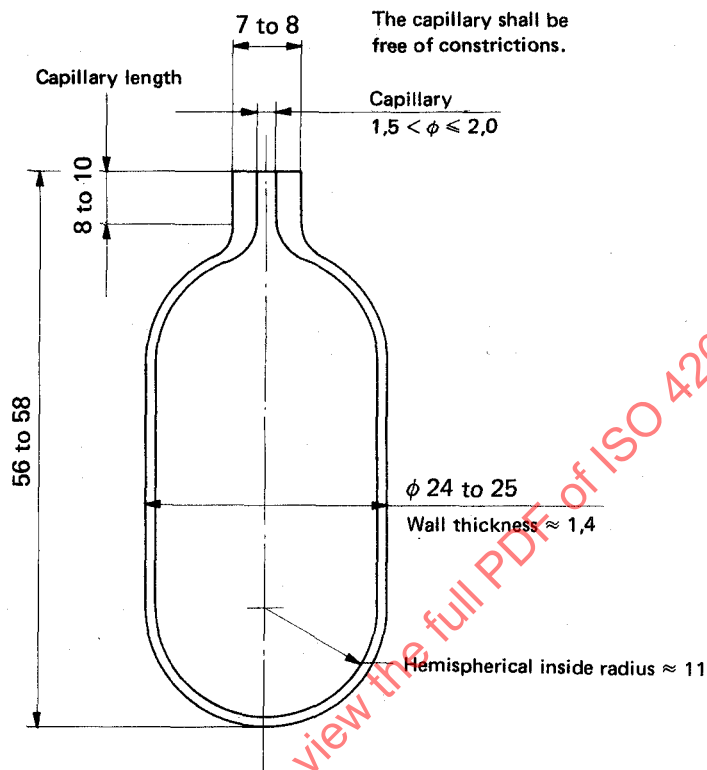


FIGURE 1 — Glass coking bulb

4.2 Control bulb, stainless steel, containing a thermocouple and conforming to the dimensions and tolerances shown in figure 2, for use in determining compliance of furnace characteristics with the performance requirements (see clause 5). The control bulb shall be provided with a dull finish, by heating in a furnace at a temperature of 850 to 900 °C for 30 min, and shall not be polished thereafter. 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 Test portion charging syringe, 5 or 10 ml glass hypodermic syringe fitted with a needle of 1,5 mm outside diameter or a serum needle of 1,45 to 1,47 mm outside diameter, for transfer of the test portion to the glass coking bulb.

NOTE — 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. The Luer-Lok 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, of solid metal, having coking bulb wells $25,5 \pm 0,1$ 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.

NOTE — Ramsbottom coke furnaces now in use may have dimensions which differ from those given in 4.4. However, it is strongly recommended that new furnaces obtained after the adoption of this method conform to the requirements outlined in 4.4. A description of one type of furnace which has been found to be satisfactory is given in the annex.

Dimensions in millimetres

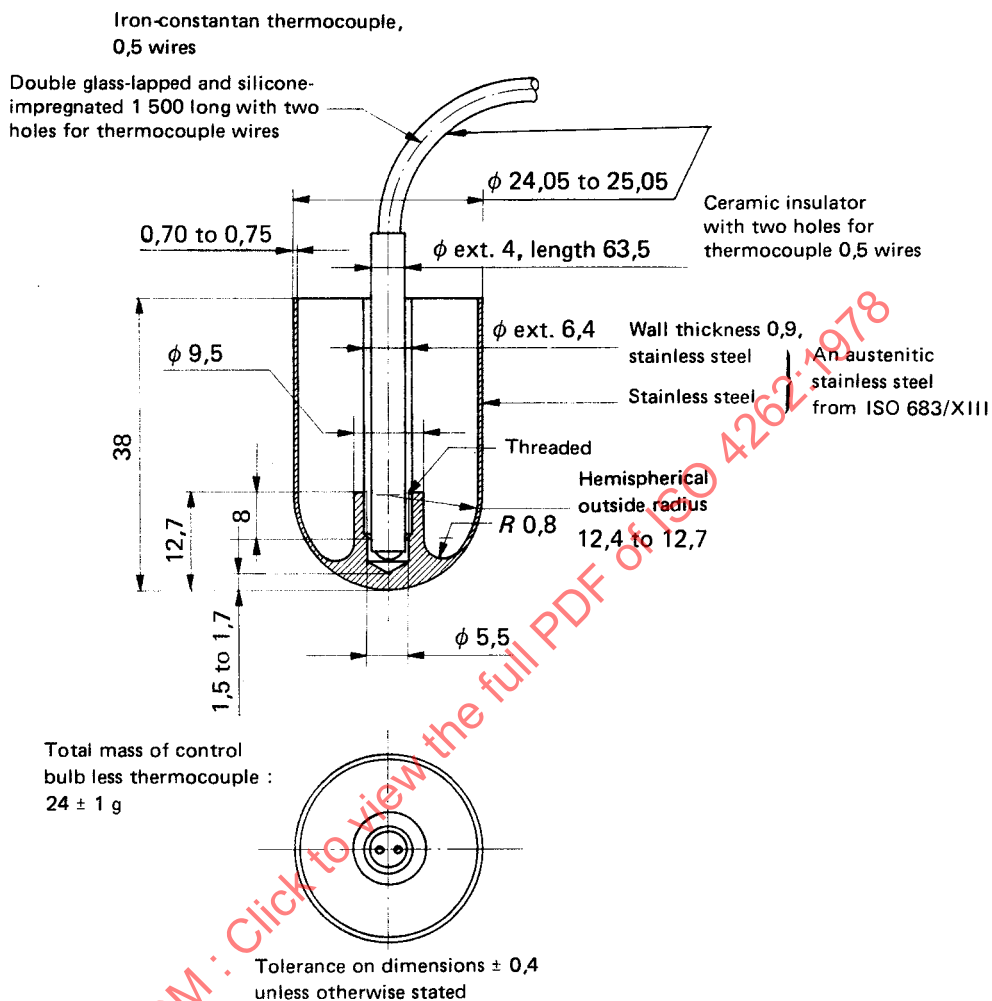


FIGURE 2 — Control bulb

4.5 Temperature-measuring devices : a removable iron-constantan thermocouple with a sensitive pyrometer, or other suitable temperature-indicating device, located centrally near the bottom portion of the furnace and arranged to measure the temperature of the furnace so that the performance tests specified in clause 5 can be carried out. It is desirable to protect the temperature indicating device with a quartz or thin metal sheath when a molten bath is used.

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

5 CHECKING PERFORMANCE OF APPARATUS

Periodically check the performance of the furnace (4.4) and temperature-measuring devices (4.5) as described in 5.1 to 5.3 to make certain that as used they conform to the requirements of the method. Consider the furnace as having

standard performance, and use it with any degree of loading, when the operating requirements described for each coking bulb well are met, while the bath is fully loaded as well as singly loaded. Use only a furnace that has successfully undergone the performance or control tests given in this clause.

5.1 Thermocouple

At least once every 50 h of use of the control bulb (4.2), calibrate the thermocouple in the control bulb against a standard thermocouple.

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

5.2 Fully loaded furnace

When the furnace temperature is within a previously chosen 2°C temperature range (which range is to be used thereafter with that particular furnace for both standard-

ization and routine operation) and within the general range $550 \pm 5^\circ\text{C}$, insert the control bulb (4.2) in one well and, within 15 s, insert in each of the other wells a glass coking bulb (4.1) containing $4 \pm 0,1\text{ g}$ of a viscous neutral petroleum lubricating oil with a viscosity within the range 60 to $100\text{ mm}^2/\text{s}^*$ 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 and not more than 6 min from the instant of its insertion in the furnace, and remains within the range $550 \pm 3^\circ\text{C}$ 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 similar fashion with the furnace fully loaded each time.

5.3 Singly loaded furnace

When the furnace temperature is within a previously chosen 2°C temperature range (which range is to be used thereafter with that particular furnace for both standardization and routine operation) and within the general range $550 \pm 5^\circ\text{C}$, insert the control bulb (4.2) in one well, with the remaining wells unoccupied. 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 and not more than 6 min from the instant of its insertion in the furnace, and remains within the range $550 \pm 3^\circ\text{C}$ 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 similar fashion with the furnace singly loaded each time.

NOTE — It is possible that not all of the wells in old furnaces will meet the requirements when fully loaded and singly loaded; 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 can be used at any one time, the three wells to be used should be chosen from the performance data obtained with fully loaded and singly loaded furnaces. Then each of the three wells should be checked 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 PROCEDURE

6.1 Place a new glass coking bulb (4.1) (see note) in the coking furnace (4.4) at 550°C for about 20 min to decompose any foreign organic matter and to remove water. Place the bulb in a closed desiccator over calcium

chloride or silica gel for 20 to 30 min and then weigh to the nearest 0,1 mg.

NOTE — Do not re-use a glass coking bulb, as unpredictable results are sometimes obtained in such cases. For routine testing, new bulbs may be used without pre-ignition provided that they are visibly free from particles or other contamination. All new bulbs should be heated in an oven to 150°C , placed in a desiccator, and then weighed to the nearest 0,1 mg.

6.2 Shake thoroughly the sample to be tested, first warming if necessary to reduce its viscosity. Strain the sample through a $150\text{ }\mu\text{m}$ 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 the table. Make sure 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 1 mg. If difficulty is encountered in loading very viscous or asphaltic test portions, of whatever size, into the glass coking bulb, the apparatus shown in the annex may be used.

NOTE — 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 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 rubber 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. It is necessary to use tubing with the same internal diameter as that of the neck of the coking bulb to prevent accumulation of any sediment during transfer.

6.3 Place the coking bulb in a "standard performance well" with the furnace at the checking temperature (see note 1), and allow to remain for 20 ± 2 min. Remove the bulb with metal tongs, the tips of which have just been heated. Reproduce the furnace and bulb conditions used when standardizing that bulb well (see clause 5 and note to 5.3). If there is appreciable loss of oil from frothing, discard the test and repeat the determination using a smaller test portion (see note 2).

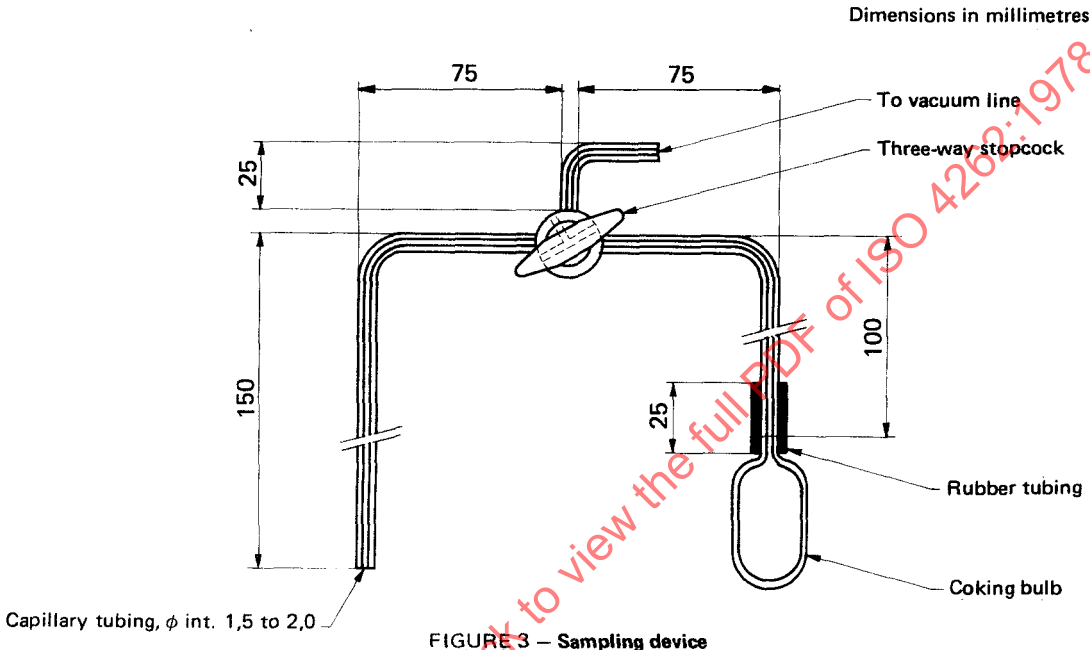
NOTES

1 On making 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 $553 \pm 1^\circ\text{C}$ when inserting the control bulb (4.2), then it is necessary to use similar temperature conditions in the

* In the SI system the unit of kinematic viscosity is the m^2/s , but for practical use a sub-multiple is more convenient. The centistokes (cSt) is $10^{-6}\text{ m}^2/\text{s}$ ($= 1\text{ mm}^2/\text{s}$) and is customarily used.

TABLE — Test portion mass

Ramsbottom carbon residue	Test portion mass
%	g
Less than 6,0	4,0 ± 0,1
6,0 to 14,0	1,0 ± 0,1
14,1 to 20,0	0,5 ± 0,1



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 inappreciable.

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

6.4 After removal, cool the bulb in a desiccator under the same conditions (including time for weighing) used before filling the bulb (see 6.2). 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 — 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, with the results, such findings as : coke more or less fills the bulb;

liquid material is present, either as limpid residue or drops; the residue is not black and flaky, but is coloured and pulverulent (presumably from presence of inorganic materials).

7 MODIFIED PROCEDURE FOR DETERMINATION ON A 10 % DISTILLATION RESIDUE

This procedure is applicable to products having a Ramsbottom carbon residue less than 0,1 % before distillation.

7.1 Procedure using a 200 ml test portion

7.1.1 Assemble the distillation apparatus described in ISO 3405, except that a 250 ml distillation flask (see figure 4) and a 200 ml measuring cylinder (see figure 5) shall be used.

A thermometer is not essential but the use of the high temperature range thermometer specified in ISO 3405 is recommended.

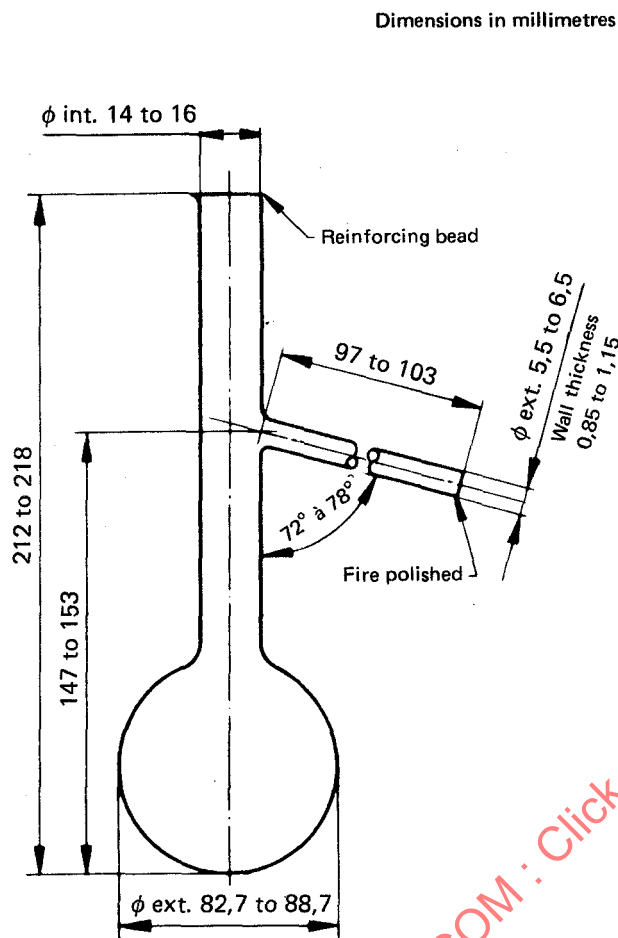


FIGURE 4 – 250 ml distillation flask

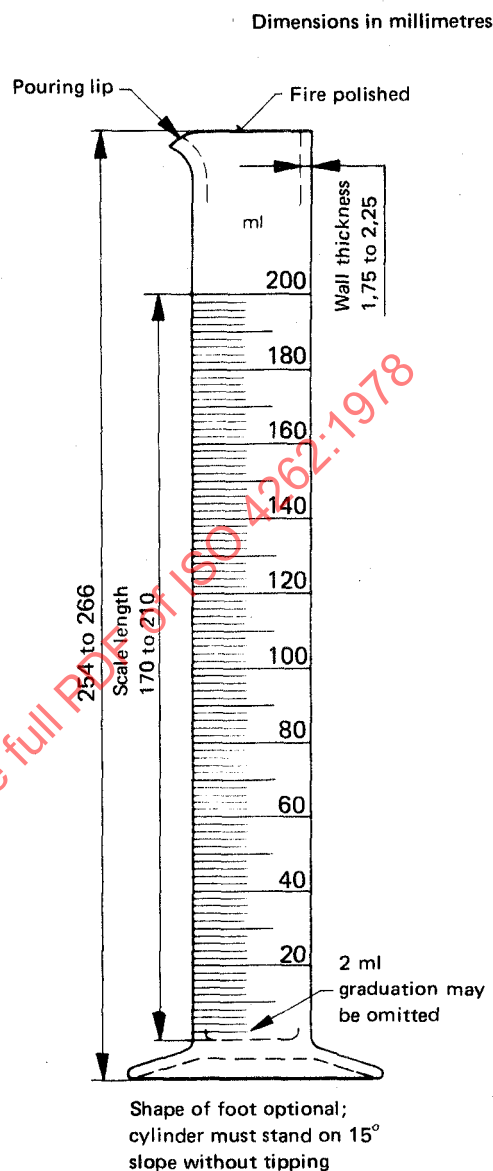


FIGURE 5 – 200 ml measuring cylinder

7.1.2 Place a volume of sample equivalent to 200 ml at 13 to 18 °C in the flask. Maintain the condenser bath at 0 to 4 °C; for some oils it may be necessary to maintain the temperature between 38 and 60 °C to avoid solidification of waxy material in the condenser tube. 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.

7.1.3 Apply heat to the flask at a uniform rate so regulated that the first drop of condensate falls from the condenser 10 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 to 10 ml per min. Continue the distillation until 178 ± 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.

7.1.4 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 represent a 10 % distillation residue from the original product.

7.1.5 While the distillation residue is warm enough to flow freely, place $4,0 \pm 0,1$ g of it into the previously weighed coking bulb (4.1). The hypodermic syringe (4.3) provides a convenient means of performing this operation. After cooling, weigh the bulb and contents to the nearest 1 mg, and carry out the carbon residue test in accordance with the procedure described in clause 6.

7.2 Alternative procedure using a 100 ml test portion

7.2.1 Assemble the distillation apparatus described in ISO 3405.

A thermometer is not essential but the use of the high temperature range thermometer specified in ISO 3405 is recommended.

7.2.2 Proceed as in 7.1.2 except that a volume of sample equivalent to 100 ml at 13 to 18 °C is placed in a flask.

7.2.3 Proceed as in 7.1.3 except that the distillation shall be continued until $89 \pm 0,5$ ml has been collected, and that the condenser shall be allowed to drain until 90 ml (90 % of the charge in the flask) has been collected in the cylinder.

7.2.4 Continue the 10 % residue procedure as described in 7.1.4 and 7.1.5.

8 EXPRESSION OF RESULTS

Calculate the carbon residue of the sample or of the 10 % distillation residue, as a percentage by mass, as follows :

$$\frac{m_1}{m_0} \times 100$$

where

m_0 is the mass, in grams, of test portion;

m_1 is the mass, in grams, of carbon residue.

9 PRECISION

The precision of the method, as obtained by statistical examination of inter-laboratory test results, is as follows :

9.1 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 values shown in figure 6 only in one case in twenty.

9.2 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 values shown in figure 6 only in one case in twenty.

10 TEST REPORT

Report the value obtained, as a percentage by mass [% (m/m)], as "Ramsbottom carbon residue" or as "Ramsbottom carbon residue on 10 % distillation residue" or "Ramsbottom carbon residue on 10 % distillation residue (100 ml test portion)" with reference to this International Standard. When a reduced size of test portion has been used, report the mass taken.

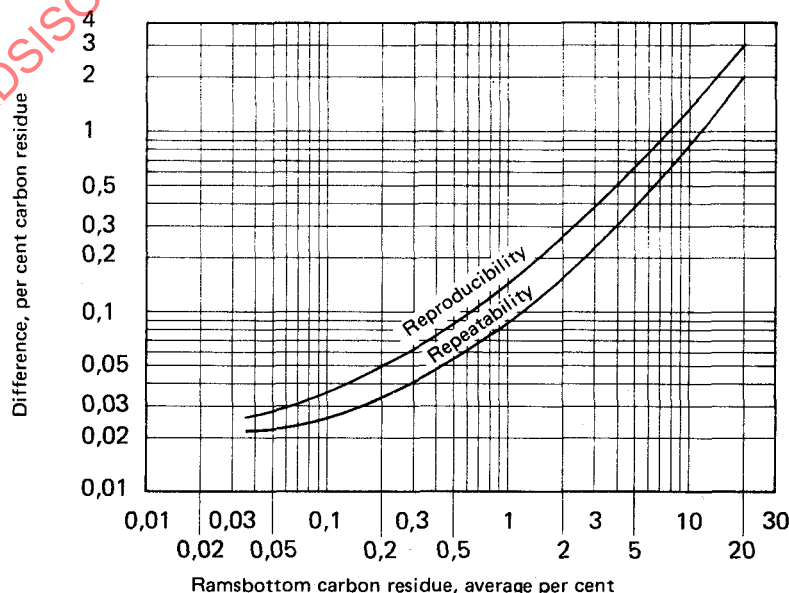


FIGURE 6 — Precision data