INTERNATIONAL
STANDARD

ISO
1656

Third edition
1996-02-01

Rubber, raw natural, and rubber latex, natural — Determination of nitrogen content

Caoutchouc brut naturel et latex de caoutchouc naturel — Dosage de l'azote

Reference number
ISO 1656:1996(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 1656 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products.*

This third edition cancels and replaces the second edition (ISO 1656:1988), which has been technically revised.

Annex A of this International Standard is for information only.

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Rubber, raw natural, and rubber latex, natural — Determination of nitrogen content

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies a macro-method and a semi-micro method for the determination of nitrogen in raw natural rubber and in natural rubber latex using variants of the Kjeldahl process.

NOTE 1 The determination of nitrogen in natural rubber is usually carried out in order to arrive at an estimate of the protein content. Minor amounts of non-proteinous nitrogen-containing constituents are also present, however, and in the dry solids prepared from natural rubber latex these materials can make a substantial contribution to the total nitrogen content.

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 123:1985, *Rubber latex — Sampling.*

ISO 124:1992, *Rubber latices — Determination of total solids content.*

ISO 1795:1992, *Rubber, raw, natural and synthetic — Sampling and further preparative procedures.*

ISO/TR 9272:1986, *Rubber and rubber products — Determination of precision for test method standards.*

3 Principle

A known mass of the sample is digested with a mixture of sulfuric acid, potassium sulfate, and catalytic amounts of copper sulfate and selenium or sodium selenate, thereby converting nitrogen compounds into ammonium hydrogen sulfate from which the ammonia is distilled after making the mixture alkaline.

The distilled ammonia is absorbed

- either in standard volumetric sulfuric acid solution followed by titration of the excess acid with a standard volumetric base solution;
- or in boric acid solution followed by titration with standard volumetric acid solution (as boric acid is a weak acid, it does not affect the indicator used for this titration).

4 Macro-method

4.1 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1.1 Catalyst mixture or catalyst solution.

CAUTION — When working with selenium, avoid breathing vapours and/or contact with skin or clothing. Work only with adequate ventilation.

4.1.1.1 Catalyst mixture

Prepare a finely divided intimate mixture of

- 30 parts by mass of anhydrous potassium sulfate (K_2SO_4);
- 4 parts by mass of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$);
- 1 part by mass of selenium powder, or 2 parts by mass of sodium selenate decahydrate ($Na_2SeO_4 \cdot 10H_2O$).

4.1.1.2 Catalyst solution

Dissolve, with heating,

- 110 g of anhydrous potassium sulfate,
- 14,7 g of copper sulfate pentahydrate,
- 3,7 g of selenium, or 7,49 g of sodium selenate,

in 600 cm^3 of sulfuric acid (4.1.2).

4.1.2 Sulfuric acid, ρ 1,84 g/cm^3.

4.1.3 Sulfuric acid, standard volumetric solution, $c(H_2SO_4)$ = 0,05 mol/dm^3.

4.1.4 Sodium hydroxide, standard volumetric solution, c(NaOH) = 0,1 mol/dm^3.

4.1.5 Sodium hydroxide, solution, c(NaOH) ≈ 10 mol/dm^3.

Dissolve 400 g of solid sodium hydroxide in 600 cm^3 of water.

4.1.6 Boric acid, solution, $c(H_3BO_3) \approx$ 0,17 mol/dm^3.

Dissolve 40 g of solid boric acid in 1 dm^3 of water, warming if necessary, and cool the solution to room temperature.

4.1.7 Mixed indicator, solution.

Dissolve 0,1 g of methyl red and 0,05 g of methylene blue in 100 cm^3 of 96 % (*V/V*) ethanol.

This indicator may deteriorate during storage and shall therefore be freshly prepared.

4.2 Apparatus

Ordinary laboratory apparatus and

Kjeldahl apparatus, with a digestion flask of capacity 800 cm^3.

4.3 Sampling and preparation of test portion

For the determination of nitrogen in raw solid rubber, a test portion shall be taken from the homogenized piece, sampled and prepared in accordance with ISO 1795.

For the determination of nitrogen in latex, a representative portion (see ISO 123) of thoroughly mixed latex containing about 2 g of total solids shall be dried to constant mass as specified in ISO 124.

4.4 Procedure

4.4.1 Cut about 2 g of the rubber or dried latex, weighed to the nearest 0,5 mg, into small pieces and place in the digestion flask (see 4.2). Add about 13 g of the catalyst mixture (4.1.1.1) and 60 cm^3 of the sulfuric acid (4.1.2), or, alternatively, 65 cm^3 of the catalyst solution (4.1.1.2). Mix the contents of the flask by swirling, and then boil gently until the solution is clear. Continue boiling for a further 1 h.

Allow the digestion flask and its contents to cool to room temperature, cautiously add 200 cm^3 of water and mix by swirling.

Place the receiving flask containing the absorbing solution in position, connect the distillation unit, then slowly add 150 cm^3 of the sodium hydroxide solution (4.1.5) to the digestion flask from a dropping funnel.

4.4.2 Carry out the absorption and titration of the liberated ammonia by the procedure described in 4.4.2.1 or 4.4.2.2. The temperature of the receiving flask shall be maintained below 30 °C to prevent any loss of ammonia.

4.4.2.1 Place 75 cm^3 of water and, by means of a pipette, 25 cm^3 of the standard volumetric sulfuric acid solution (4.1.3) in the receiving flask of the distillation unit, together with two drops of mixed indicator solution (4.1.7). Position the receiving flask so that the end of the delivery tube from the condenser dips below the surface of the absorbing solution. While holding the stopper of the digestion flask in place, thoroughly mix the contents by swirling. Immediately commence distillation and continue at a steady rate until 200 cm^3 of distillate have been collected. If the colour of the indicator changes, indicating alkalinity of the absorbing solution, discontinue the determination and repeat the procedure using more sulfuric acid or a smaller test portion.

When the distillation is complete (normally when the volume in the flask reaches about 300 cm^3), titrate the contents with the sodium hydroxide solution (4.1.4), reading the burette to the nearest 0,02 cm^3.

4.4.2.2 Place 100 cm^3 of the boric acid solution (4.1.6) in the receiving flask of the distillation unit with two drops of the mixed indicator solution (4.1.7). Carry out the distillation as described in 4.4.2.1 and titrate the distillate with the sulfuric acid solution (4.1.3), reading the burette to the nearest 0,02 cm^3.

4.5 Blank test

In parallel with the determination, carry out a blank test using the same quantities of reagents under the same operating conditions, but omitting the test portion.

4.6 Expression of results[1)]

4.6.1 When sulfuric acid is used as the absorbing solution as specified in 4.4.2.1, the nitrogen content of the rubber, expressed as a percentage by mass, is given by the formula

$$\frac{0,14(V_2 - V_1)}{m}$$

where

V_1 is the volume, in cubic centimetres, of sodium hydroxide solution (4.1.4) required for the titration;

V_2 is the volume, in cubic centimetres, of sodium hydroxide solution (4.1.4) required for the titration in the blank test;

m is the mass, in grams, of the test portion.

Express the result to the nearest 0,01 %.

4.6.2 When boric acid is used as the absorbing solution as specified in 4.4.2.2, the nitrogen content of the rubber, expressed as a percentage by mass, is given by the formula

$$\frac{0,14(V_3 - V_4)}{m}$$

where

V_3 is the volume, in cubic centimetres, of sulfuric acid solution (4.1.3) required for the titration;

V_4 is the volume, in cubic centimetres, of sulfuric acid solution (4.1.3) required for the titration in the blank test;

m is the mass, in grams, of the test portion.

Express the result to the nearest 0,01 %.

5 Semi-micro method

5.1 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.1.1 Catalyst mixture.

CAUTION — When working with selenium, avoid breathing vapours and/or contact with skin or clothing. Work only with adequate ventilation.

Prepare a finely divided intimate mixture of

- 30 parts by mass of anhydrous potassium sulfate (K_2SO_4);
- 4 parts by mass of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$);
- 1 part by mass of selenium powder, or 2 parts by mass of sodium selenate decahydrate ($Na_2SeO_4 \cdot 10H_2O$).

5.1.2 Sulfuric acid, ρ 1,84 g/cm^3.

5.1.3 Sulfuric acid, standard volumetric solution, $c(H_2SO_4) = 0,01$ mol/dm^3.

5.1.4 Sodium hydroxide, solution, $c(NaOH) \approx 10$ mol/dm^3.

Dissolve 400 g of solid sodium hydroxide in 600 cm^3 of water.

5.1.5 Sodium hydroxide, standard volumetric solution, $c(NaOH) = 0,02$ mol/dm^3, carbonate-free.

5.1.6 Boric acid, solution, $c(H_3BO_3) \approx 0,17$ mol/dm^3.

Dissolve 40 g of solid boric acid in 1 dm^3 of water, warming if necessary, and cool the solution to room temperature.

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1) If the concentrations of the standard volumetric solution used are not exactly as specified in the list of reagents, appropriate corrections should be made.

5.1.7 Mixed indicator, solution.

Dissolve 0,1 g of methyl red and 0,05 g of methylene blue in 100 cm^3 of 96 % (*V*/*V*) ethanol.

This indicator may deteriorate during storage and shall therefore be freshly prepared.

5.2 Apparatus

Ordinary laboratory apparatus and

5.2.1 Semi-micro Kjeldahl digestion apparatus, with digestion flasks of capacity 30 cm^3 and 10 cm^3 (for an example of a typical apparatus, see figures 1, 2 and 3).

5.2.2 Semi-micro Kjeldahl distillation unit, with a condenser tube of silver, borosilicate glass or tin (for an example, see figures 4 to 9).

5.2.3 Semi-micro burette, of capacity 5 cm^3 or 10 cm^3, graduated in 0,02 cm^3 divisions.

5.3 Sampling and preparation of test portion

For the determination of nitrogen in raw solid rubber, a test portion shall be taken from the homogenized piece, sampled and prepared in accordance with ISO 1795.

For the determination of nitrogen in latex, a representative portion (see ISO 123) of thoroughly mixed latex containing about 0,1 g of total solids shall be dried to constant mass as specified in ISO 124.

5.4 Procedure

5.4.1 Weigh, to the nearest 0,1 mg, 0,1 g to 0,2 g of the rubber or dried latex and place in a digestion flask (see 5.2.1). Add about 0,65 g of the catalyst mixture (5.1.1) and 3,0 cm^3 of the sulfuric acid (5.1.2) and heat the contents carefully to the boiling point. Continue boiling for a further 30 min after the digest has become clear and green with no yellow tint.

Avoid excess boiling, as indicated by a tendency for the digest to solidify on cooling, since this may lead to loss of nitrogen.

Bring the water in the steam generator of the distillation unit to the boil and pass steam through the distillation apparatus (5.2.2), including the receiving flask, for at least 2 min. The water-jacket of the condenser shall be empty of water during the steaming-out operation. Meanwhile, cool the digestion flask to room temperature or below, add 10 cm^3 of water and immediately transfer the contents to the distillation flask at the conclusion of the steaming-out process. Complete the transfer by rinsing three times with 3 cm^3 portions of water and draining the flask thoroughly after each transfer.

5.4.2 Discard any condensate which has collected in the receiver and complete the distillation and titration of ammonia by the procedure described in 5.4.2.1 or 5.4.2.2. The temperature of the receiving flask shall be maintained below 30 °C to prevent loss of ammonia.

5.4.2.1 Add from the semi-micro burette (5.2.3) to the steamed-out receiver of the distillation apparatus a measured volume of sulfuric acid solution (5.1.3), using at least 5 cm^3 (the exact volume depending on the amount of nitrogen expected), together with two drops of the mixed indicator solution (5.1.7) and about 5 cm^3 of water. Position the receiver so that the end of the delivery tube from the condenser dips below the surface of the acid. It is an advantage to tilt the receiver slightly to gain a greater depth of liquid.

Add approximately 15 cm^3 of the sodium hydroxide solution (5.1.4) to the distillation flask by means of a measuring cylinder, and pass steam from the generator through the distillation flask for 10 min to 12 min at such a rate that the final volume of liquid in the receiver is about 70 cm^3. If the colour of the indicator changes, indicating alkalinity of the absorbing solution, discontinue the determination and repeat the procedure using more sulfuric acid or a smaller test portion.

When the distillation is complete, lower the receiving flask until the tip of the condenser is above the level of the acid, continue the distillation for another 1 min, and then rinse the tip of the condenser tube with a few cubic centimetres of water which shall be collected in the distillate. Immediately titrate the contents of the receiving flask with the sodium hydroxide solution (5.1.5), reading the burette to the nearest 0,02 cm^3.

5.4.2.2 Place about 10 cm^3 of the boric acid solution (5.1.6) in the steamed-out receiving flask with two drops of the mixed indicator solution (5.1.7). Carry out the distillation as described in 5.4.2.1, but note that, in the presence of boric acid, the indicator colour should change immediately distillation of ammonia commences. Titrate the distillate with sulfuric acid solution (5.1.3), reading the burette to the nearest 0,02 cm^3.

5.5 Blank test

In parallel with the determination, carry out a blank test using the same quantities of reagents under the same operating conditions, but omitting the test portion.

5.6 *Expression of results*[2)]

5.6.1 When sulfuric acid is used as the absorbing solution as specified in 5.4.2.1, the nitrogen content of the rubber, expressed as a percentage by mass, is given by the formula

$$\frac{0{,}028(V_2 - V_1)}{m}$$

where

V_1 is the volume, in cubic centimetres, of sodium hydroxide solution (5.1.5) required for the titration;

V_2 is the volume, in cubic centimetres, of sodium hydroxide solution (5.1.5) required for the titration in the blank test;

m is the mass, in grams, of the test portion.

Express the result to the nearest 0,01 %.

5.6.2 When boric acid is used as the absorbing solution as specified in 5.4.2.2, the nitrogen content of the rubber, expressed as a percentage by mass, is given by the formula

$$\frac{0{,}028(V_3 - V_4)}{m}$$

where

V_3 is the volume, in cubic centimetres, of sulfuric acid solution (5.1.3) required for the titration;

V_4 is the volume, in cubic centimetres, of sulfuric acid solution (5.1.3) required for the titration in the blank test;

m is the mass, in grams, of the test portion.

Express the result to the nearest 0,01 %.

6 Precision

6.1 General

The precision calculations to express repeatability and reproducibility were performed in accordance with ISO/TR 9272. Consult this Technical Report for precision concepts and nomenclature. Annex A of this International Standard gives guidance on the use of repeatability and reproducibility.

6.2 *Precision details*

6.2.1 An interlaboratory test programme was organized in late 1984 by the Rubber Research Institute of Malaysia. Two separate programmes were conducted, one in March and one in July. Two types of material were sent to each laboratory:

a) blended samples of two rubbers "A" and "B";

b) unblended (normal) samples of the same two materials "A" and "B".

6.2.2 For both the blended and the unblended samples, a test result was taken as the mean of three separate determinations.

6.2.3 The semi-micro method was used to determine the nitrogen content.

6.2.4 A "type 1" precision was measured in the interlaboratory test programme. The time period for repeatability and reproducibility was on a scale of days. A total of 14 laboratories participated in the programme for blended samples and a total of 13 laboratories in the programme for unblended samples.

6.3 Precision results

The precision results for the blended-sample programme are given in table 1 and the results for the unblended-sample programme in table 2.

7 Test report

The test report shall include the following information:

a) a reference to this International Standard and the method used;

b) all details necessary for the identification of the material tested;

c) the results and the units in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or in the International Standards to which reference is made, and any operation regarded as optional;

f) the date of the test.

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2) If the concentrations of the standard volumetric solutions used are not exactly as specified in the list of reagents, appropriate corrections should be made.

Table 1 — Type 1 precision — Blended-sample testing

Rubber sample	Average nitrogen content	Within-laboratory repeatability		Interlaboratory reproducibility	
	% (*m*/*m*)	*r*	(*r*)	*R*	(*R*)
A	0,45	0,053	11,7	0,094	20,9
B	0,53	0,024	4,45	0,161	30,2
Pooled values	0,49	0,042	8,42	0,127	25,6

r = repeatability, in percent by mass
(*r*) = repeatability, in percent (relative) of the average
R = reproducibility, in percent by mass
(*R*) = reproducibility, in percent (relative) of the average

Table 2 — Type 1 precision — Unblended-sample testing

Rubber sample	Average nitrogen content	Within-laboratory repeatability		Interlaboratory reproducibility	
	% (*m*/*m*)	*r*	(*r*)	*R*	(*R*)
A	0,36	0,021	5,83	0,189	52,7
B	0,36	0,038	10,82	0,185	51,9
Pooled values	0,36	0,031	8,67	0,187	52,4

See table 1 for symbol definitions.

Dimensions in millimetres[3)]

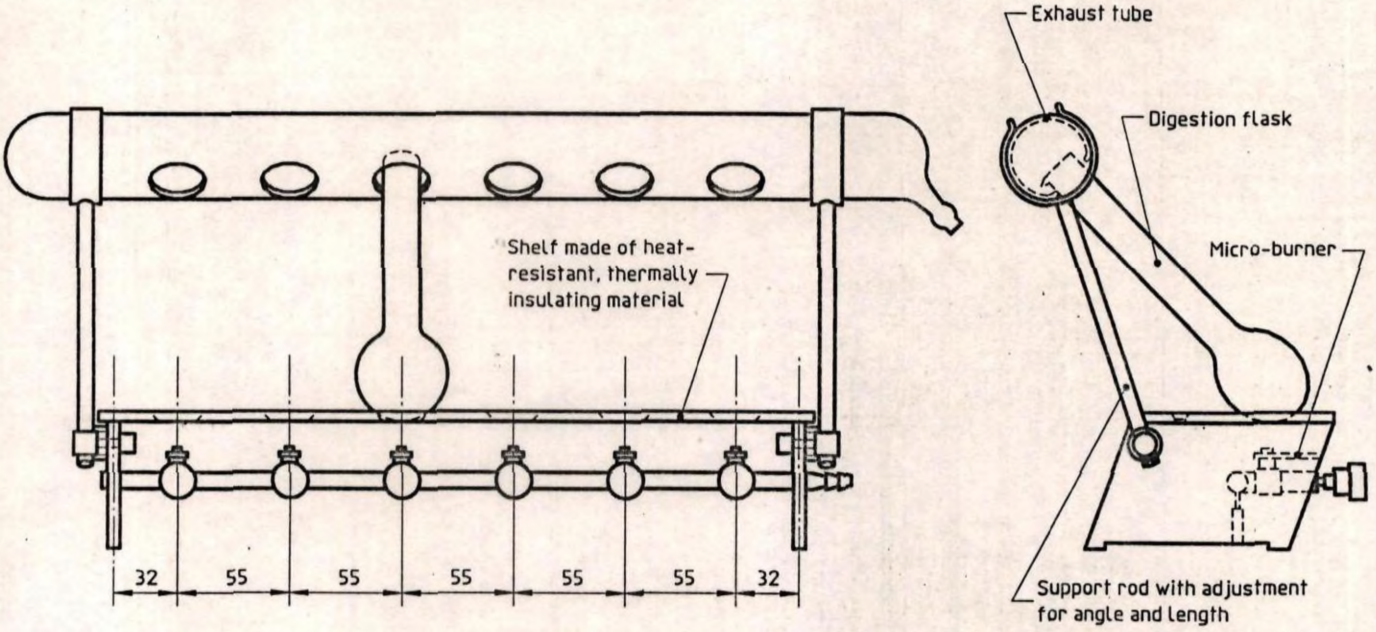

Figure 1 — Assembly of digestion apparatus for the semi-micro method

Dimensions in millimetres[3)]

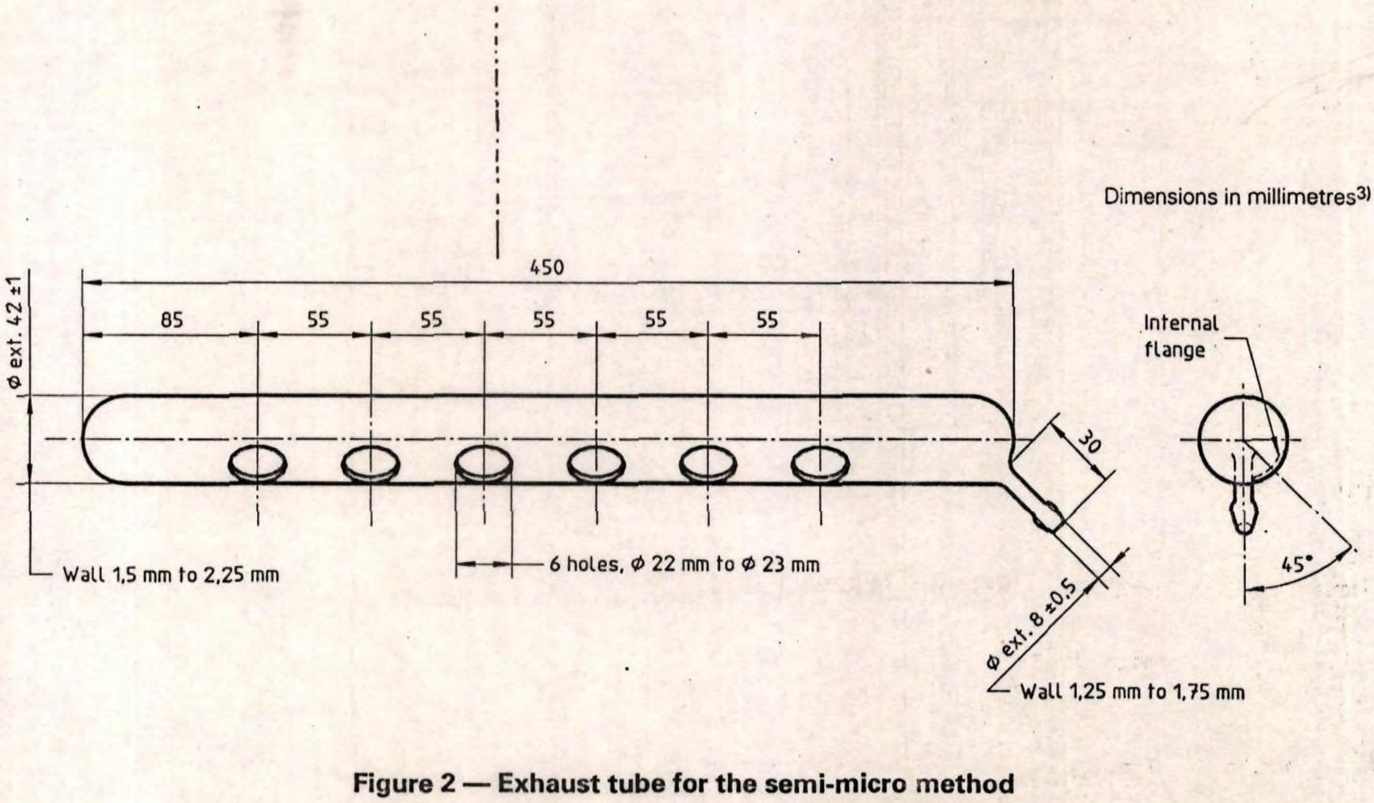

Figure 2 — Exhaust tube for the semi-micro method

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3) Where no tolerances are shown, normal working tolerances are allowed.

Dimensions in millimetres[4)]

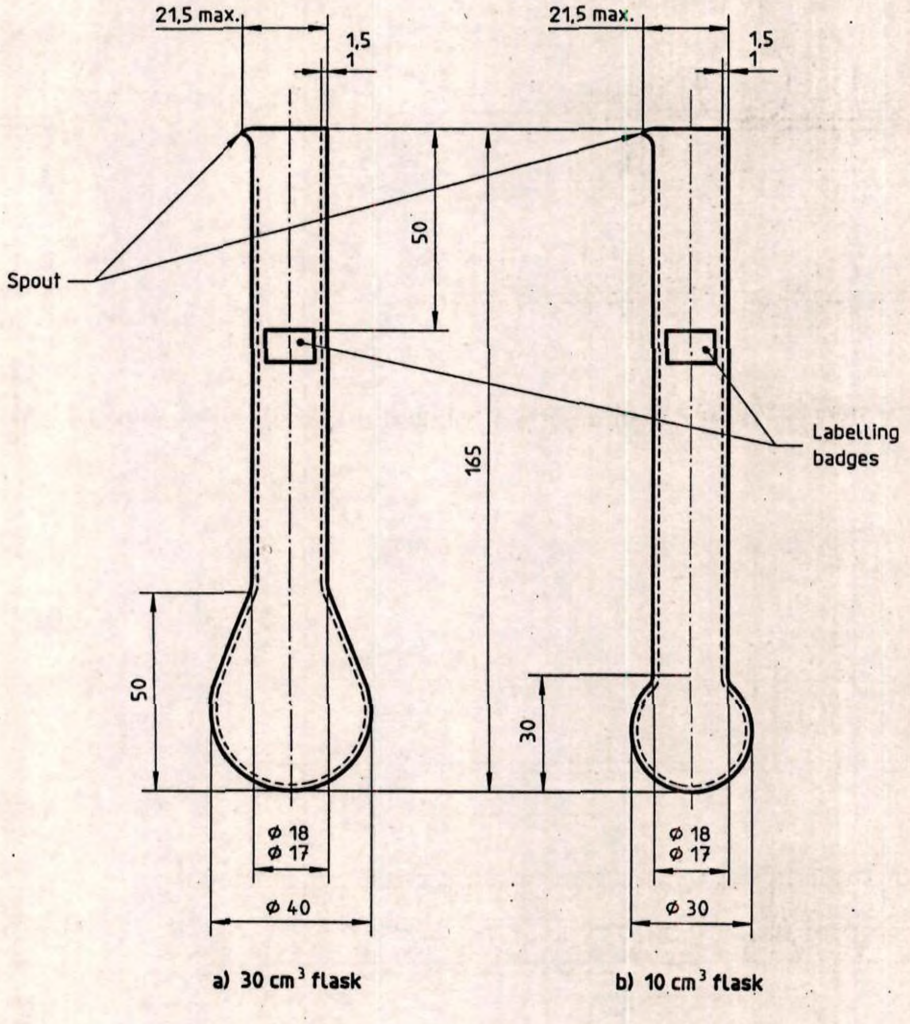

Figure 3 — Digestion flasks for the semi-micro method

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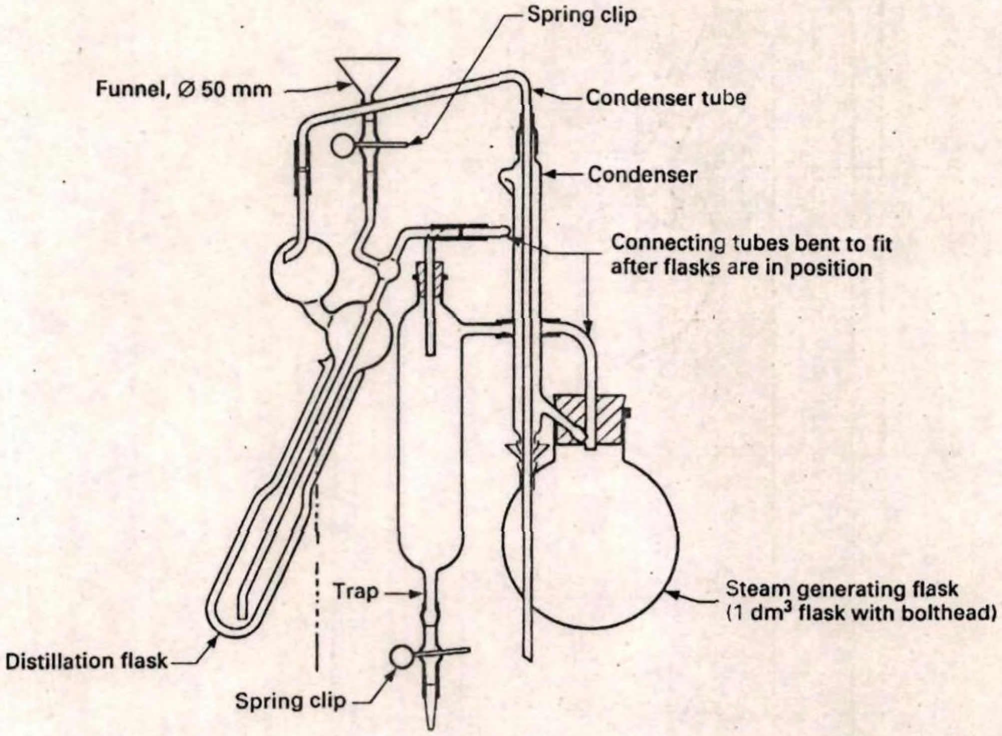
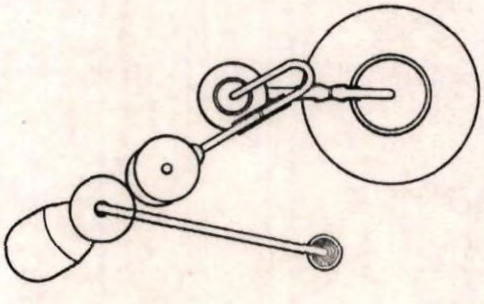
4) Where no tolerances are shown, normal working tolerances are allowed.



Elevation
(Three-quarter view as indicated by plan below)



Plan

Figure 4 — Assembly of distillation apparatus for the semi-micro method

Dimensions in millimetres[5]

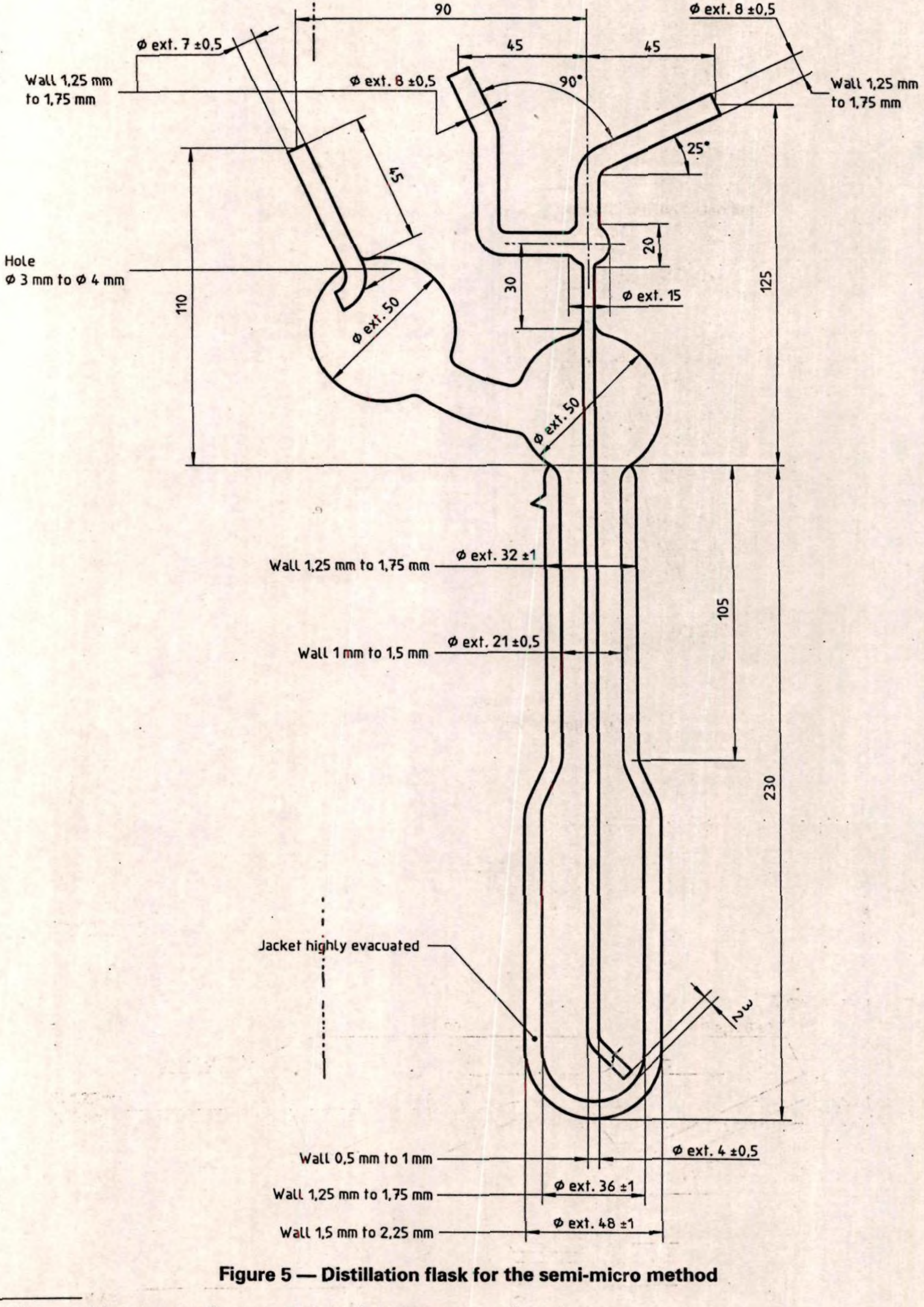


Figure 5 — Distillation flask for the semi-micro method

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[5] Where no tolerances are shown, normal working tolerances are allowed.

Dimensions in millimetres[6]

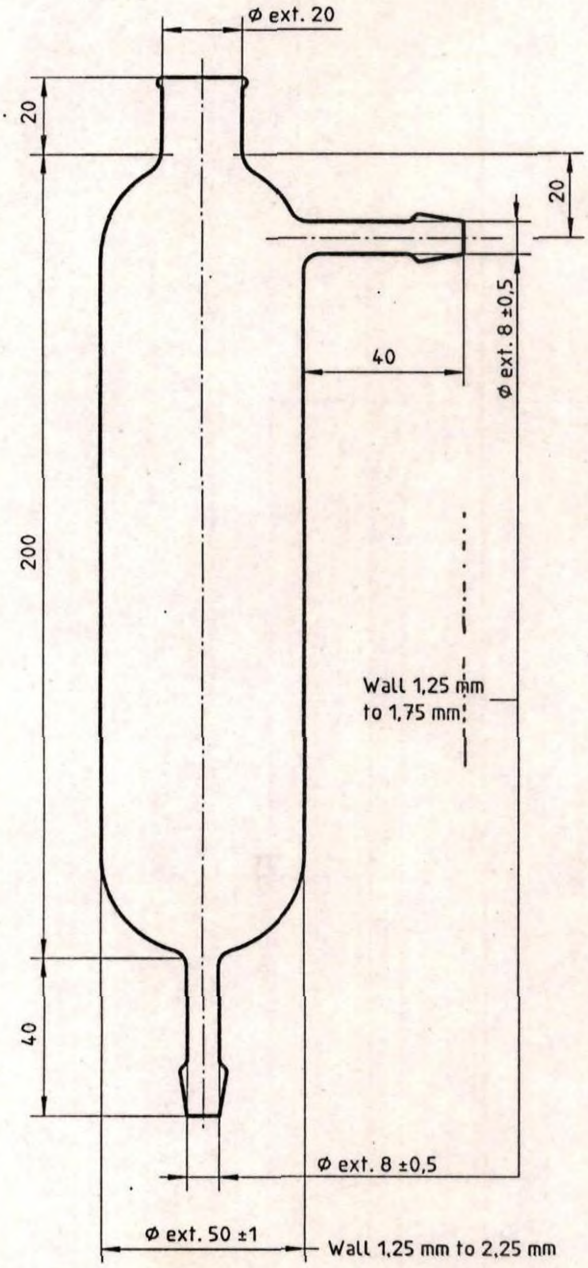

Figure 6 — Trap for the semi-micro method

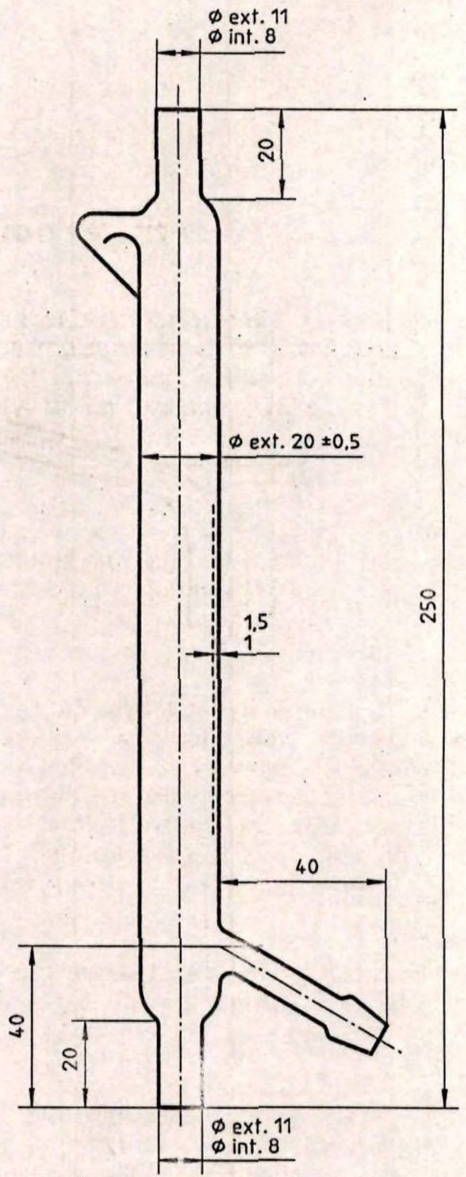

Figure 7 — Condenser jacket for the semi-micro method

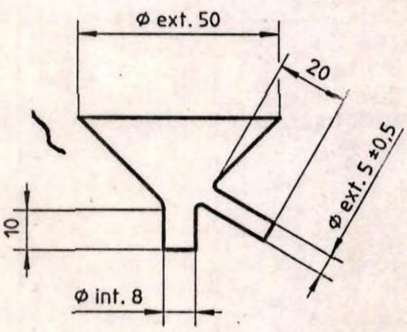

Figure 8 — Drip funnel for the semi-micro method

Where no tolerances are shown, normal working tolerances are allowed.

Dimensions in millimetres[7]

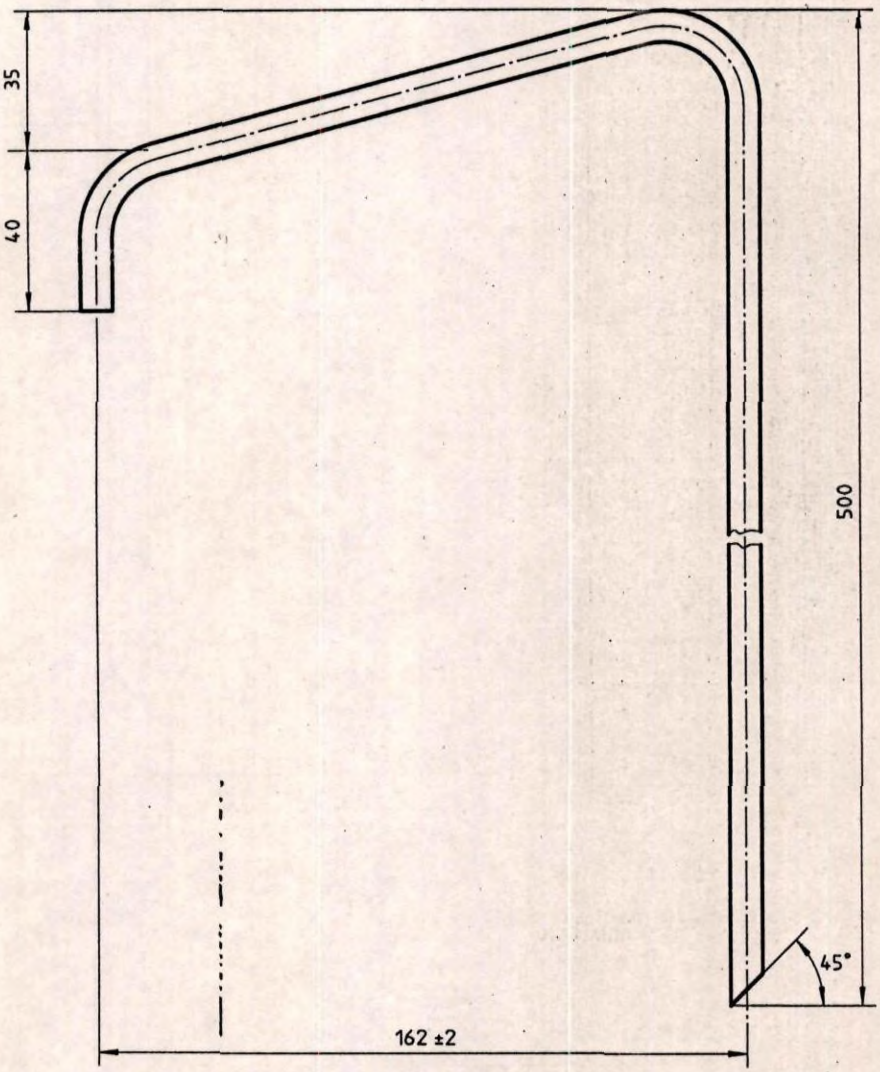

Figure 9 — Condenser tube for the semi-micro method

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[7] Where no tolerances are shown, normal working tolerances are allowed.

PCD13(2165)

Rubber, vulcanized — Determination of the effect of liquids

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard describes methods of evaluating the resistance of vulcanized thermoset or thermoplastic rubbers to the action of liquids by measurement of properties of the rubbers before and after immersion in test liquids. The liquids concerned include current service liquids, such as petroleum derivatives, organic solvents and chemical reagents as well as reference test liquids.

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 37:1994, *Rubber, vulcanized or thermoplastic — Determination of tensile stress-strain properties.*

ISO 48:1994, *Rubber, vulcanized or thermoplastic — Determination of hardness (hardness between 10 IRHD and 100 IRHD).*

ISO 175:—[1], *Plastics — Methods of test for the determination of the effects of immersion in liquid chemicals.*

ISO 471:1995, *Rubber — Temperatures, humidities and times for conditioning and testing.*

ISO 2592:—[2], *Petroleum products — Determination of flash and fire points — Cleveland open cup method.*

ISO 2977:1997, *Petroleum products and hydrocarbon solvents — Determination of aniline point and mixed aniline point.*

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

ISO 3104:1994, *Petroleum products — Transparent and opaque liquids — Determination of kinematic viscosity and calculation of dynamic viscosity.*

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[1] To be published. (Revision of ISO 175:1981)

[2] To be published. (Revision of ISO 2592:1973)

PCD13(2165)

ISO 3675:1998, *Crude petroleum and liquid petroleum products — Laboratory determination of density — Hydrometer method.* IS 1448 (Part 16).

ISO 4661-1:1993, *Rubber, vulcanized or thermoplastic — Preparation of samples and test pieces — Part 1: Physical tests.*

ISO 5661:1983, *Petroleum products — Hydrocarbon liquids — Determination of refractive index.*

3 Apparatus

3.1 **Total immersion apparatus**, designed to take account of the volatility of the test liquid and of the immersion temperature in order to prevent and minimize evaporation of the test liquid and the ingress of air.

For tests at temperatures considerably below the boiling point of the test liquid, a stoppered glass bottle or tube shall be used. For tests at temperatures near the boiling point of the test liquid, the bottle or tube shall be fitted with a reflux condenser or other suitable means of minimizing the evaporation of liquid.

The bottle or tube shall be so dimensioned that the test pieces remain completely immersed and freely exposed on all surfaces without restraint. The volume of liquid shall be at least 15 times the combined volume of the test pieces and the volume of air above the liquid shall be kept to a minimum.

The test pieces shall be mounted in jigs, preferably hanging on a rod or wire, and separated from any adjacent test piece, for instance by glass rings or other non-reactive spacers.

The materials of the apparatus shall be inert to the test liquid and to the rubber; for example materials containing copper shall not be used.

3.2 **Apparatus for testing one surface only**, which holds the test piece in contact with the liquid on only one of its surfaces.

A suitable apparatus is illustrated in figure 1. It comprises a base-plate (A) and an open-ended cylindrical chamber (B), which is held tightly against the test piece (C) by wing nuts (D) mounted on bolts (E). A hole of approximately 30 mm diameter is allowed in the base-plate for examination of the surface not in contact with the liquid. During the test, the opening on the top of the chamber shall be closed by a close-fitting plug (F).

3.3 **Balance**, accurate to 1 mg.

3.4 **Instrument for measuring the thickness of the test piece**, consisting of a micrometer dial-gauge, of adequate accuracy, firmly held in a rigid stand over a flat base-plate.

The gauge shall have a scale graduated in divisions of 0,01 mm. The plunger shall be fitted with a flat circular contact having a surface area of approximately 100 mm^2. The contact shall be perpendicular to the plunger and parallel to the base-plate. The dial-gauge shall operate to give a pressure on the rubber of approximately 2 kPa.

3.5 **Instrument for measuring the length and width of the test piece**, having a scale graduated in divisions of 0,01 mm and preferably operating without contact with the test piece, for example using an optical system.

3.6 **Instrument for measuring the change in surface area**, capable of measuring the lengths of the diagonals of the test pieces.

It shall have a scale graduated in divisions of 0,01 mm and preferably operates without contact with the test piece, for example using an optical system.

PCD 13(2165)

Dimensions in millimetres

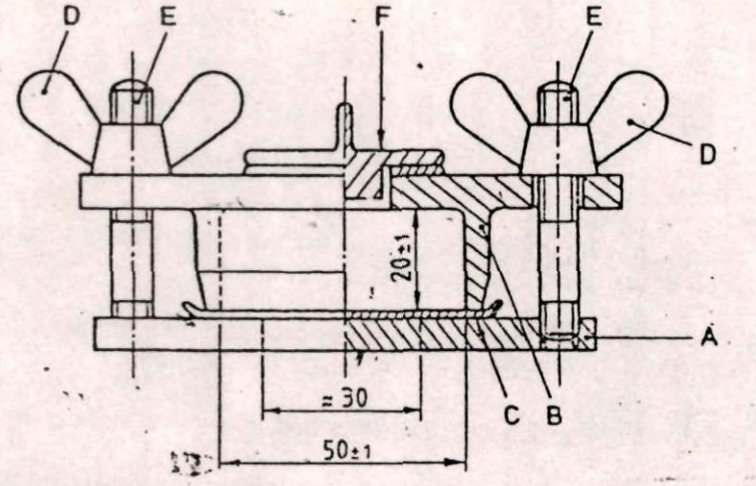

Figure 1 — Apparatus for testing one surface only

4 Test liquids

The choice of the test liquid shall depend on the purpose of the test.

When information is required on the service behaviour of a vulcanized rubber in contact with a particular liquid, then this liquid shall, if possible, be chosen for the test. Commercial liquids are not always constant in composition and the test shall, whenever practicable, include a reference material of known characteristics. Any abnormal results due to unexpected variations in the composition of the commercial liquid will thus become apparent. It may be necessary to set aside a bulk supply of the liquid for a particular series of tests.

Mineral oils and fuels are liable to vary considerably in chemical composition even when supplied at a recognized specification. The aniline point of a mineral oil gives some indication of its aromatic content and helps to characterize the action of the oil on rubber, but the aniline point alone is not sufficient to characterize a mineral oil; other things being equal, the lower the aniline point, the more pronounced the action. If a mineral oil is used as test liquid, the test report shall include the density, refractive index, viscosity and aniline point or aromatic content of the oil. For the reference mineral oils described in annex A, mineral oil raffinates are employed.

Service oils having similar fluid characteristics to the reference liquids (see annex A, clauses A.1 to A.3) will not necessarily have the same effect on the material as the reference liquids. Some fuels, particularly gasoline, vary widely in composition and, for some possible constituents, minor variations can have a large influence on the effect on rubber. Complete details of the composition of the fuel used shall therefore be included in the test report.

As commercial liquids do not always have a constant composition, a standard liquid consisting of well-defined chemical compounds or mixtures of compounds shall be used as reference liquid for the purpose of classification of vulcanized rubbers or quality control. Some suitable liquids are recommended in annex A.

When testing to determine the effect of chemical solutions, the concentration of the solution shall be appropriate to the intended use.

Ensure that the composition of the test liquid does not change significantly during immersion. The ageing of the test liquid and any interaction with the test pieces shall be taken into consideration. If there are chemically active additives in the liquid, or if there is a significant change in composition by extraction, absorption or reaction with the rubber, either the volume shall be increased, or the liquid shall be replaced with fresh liquid at specified intervals.

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5 Test pieces

5.1 Preparation

Test pieces shall be prepared in accordance with ISO 4661-1.

5.2 Dimensions

Data obtained on test pieces having different original thicknesses may not be comparable. Therefore, where possible, test pieces shall be of uniform thickness of (2 ± 0,2) mm.

Test pieces cut from commercial articles may be used. For products thinner than 1,8 mm, use the original thickness. If the material is thicker than 2,2 mm, reduce the thickness to (2 ± 0,2) mm.

Test pieces for the determination of the change in volume and mass shall have a volume of 1 cm^3 to 3 cm^3.

Test pieces for the determination of the change in hardness shall have lateral dimensions of no less than 8 mm.

Test pieces for the determination of the change in dimensions shall be quadrilateral with sides between 25 mm and 50 mm, or circular with a diameter of 44,6 mm (internal diameter of type B test piece in ISO 37). This type of test piece can also be used for the determination of mass and volume.

Test pieces for the determination of the change in surface area shall be rhomboid, with the sides cut cleanly and at right angles to the top and bottom surfaces. This can be achieved by two consecutive cuts at approximately right angles to each other, with a cutter consisting of two parallel blades, suitably spaced. The length of the sides shall be nominally 8 mm.

NOTE For the determination of the change in surface area, it may be convenient to use smaller or thinner test pieces, for example when cut from products or when rapid attainment of equilibrium is required. However, the results may not be comparable with those obtained using the specified thickness. Smaller test pieces will reduce the precision of the results.

Test pieces for the determination of tensile properties shall be in accordance with ISO 37, preferably type 2 dumb-bells. This type of test piece can also be used when determining the changes in mass, volume or hardness.

For tests with liquid contact on one surface only, the test piece shall consist of a disc with a diameter of about 60 mm.

5.3 Time interval between vulcanization and testing

Unless otherwise specified for technical reasons, the following requirements, in accordance with ISO 471 for time intervals, shall be observed.

For all test purposes, the minimum time between vulcanization and testing shall be 16 h.

For non-product tests, the maximum time between vulcanization and testing shall be 4 weeks and, for evaluations intended to be comparable, the tests shall be carried out using, as far as possible, the same time interval.

For product tests, whenever possible, the time between vulcanization and testing shall not exceed 3 months. In other cases, tests shall be made within 2 months of the date of receipt of the product by the customer.

5.4 Conditioning

Test pieces for test in the "as received" condition shall be conditioned for not less than 3 h at one of the standard laboratory temperatures specified in ISO 471. The same temperature shall be used throughout any test or any series of tests intended to be comparable.

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6 Immersion in the test liquid

6.1 Temperature

The immersion shall preferably be carried out at one or more of the temperatures listed in 4.3.2 of ISO 471:1995.

As elevated temperatures may greatly increase the oxidation of the rubber, volatilization or decomposition of the immersion liquid and the effect of any chemically active additives in the liquid (for example in service liquids), appropriate selection of the test temperatures is very important.

In tests intended to simulate service conditions, and using the actual liquid with which the rubber will be used, the test conditions shall approximate those found in service, using the closest standard temperature equal to or higher than the service temperature.

6.2 Duration

Since the rate of penetration of liquids into rubbers depends on the temperature, the type of rubber material and the type of liquid, the use of only one standard period of immersion is precluded. For acceptance purposes, it is recommended that repeated determinations be made and recorded after subsequent periods of immersion so as to indicate the change in properties with time. The total immersion time shall, if possible, extend well beyond the point of maximum absorption.

For control purposes, a single period of immersion may suffice but maximum absorption should preferably be reached. For such purposes one of the following periods shall be used:

$24^{\ 0}_{-2}$ h　　$72^{\ 0}_{-2}$ h

7 days ± 2 h　　Multiples of 7 days ± 2 h.

NOTE 1 Since the amount of liquid absorbed is initially proportional to the square root of time rather than time itself, it is helpful to assess the "time to maximum absorption" by plotting the amount absorbed against the square root of time.

NOTE 2 The percentage change during the early stages of immersion is inversely proportional to the test piece thickness. Therefore, lower tolerances for thickness are advisable to obtain consistent results when maximum absorption is not reached.

7 Procedure

7.1 General

Use three test pieces for each set of measurements and make any identification marks required before immersion.

Immerse the test pieces in the appropriate apparatus described in 3.1 or 3.2 using the liquid selected (see clause 4) and the temperature selected (see 6.1)

For total immersion, place the specimens at a distance of at least 5 mm from the sides of the container and at least 10 mm from the bottom and top surfaces. If the density of the rubber is less than that of the liquid, means shall be provided for holding the test pieces completely below the surface of the liquid.

The ingress of air shall be avoided. If the influence of air is to be tested, the degree of access of air may be determined by agreement between the interested parties.

At the end of the period of immersion, bring the test pieces, if necessary, to the standard laboratory temperature within 30 min. This can be done by quickly transferring the test pieces to a fresh portion of the test liquid at this temperature for a period of 10 min to 30 min.

Remove surplus test liquid from the surface. When volatile liquids are used, remove and quickly wipe the test pieces with a filter paper or a piece of fabric which does not deposit lint. Viscous non-volatile liquids can be removed by filter paper and, if necessary, by quickly immersing the test piece in a volatile liquid, such as methanol or petroleum ether, then quickly wiping it.

Following removal of the test pieces from volatile test liquids, it is important that each subsequent manipulatio takes place as soon as possible. Carry out the tests immediately after the removal of surplus liquid or, for change i mass or volume, by placing the test piece immediately in a weighing bottle.

If, after the measurement of mass or dimensions, the same test pieces are used for the measurement of other properties, immerse the test pieces in the volatile liquid again. The total immersion time shall be in accordance with 6.2. The maximum time between removal from the test liquid and the end of the measurement shall be:

— change in dimensions:	1 min;
— change in hardness:	1 min;
— tensile test:	2 min.

If the immersion is to be continued, put the test pieces back in the liquid immediately and return them to the temperature-controlled oven or bath.

The changes in properties can also be determined after drying. For this purpose, dry the test piece under an absolute air pressure of approximately 20 kPa at approximately 40 °C to constant mass, i.e. until the difference between successive weighings at 30 min intervals does not exceed 1 mg. Cool to room temperature and condition by keeping at the standard laboratory temperature for not less than 3 h.

7.2 Change in mass

Weigh each test piece to the nearest milligram at the standard laboratory temperature before and after immersion.

Calculate the percentage change in mass Δm_{100} as follows:

$$\Delta m_{100} = \frac{m_i - m_0}{m_0} \times 100 \qquad \ldots(1$$

where

m_0 is the initial mass of the test piece;

m_i is the mass of the test piece after immersion.

Report the result as the median value for the three test pieces.

7.3 Change in volume

The water displacement method is used for water-insoluble liquids.

Weigh each test piece in air to the nearest milligram (mass m_0), and then reweigh each test piece in distilled wat at the standard laboratory temperature (mass $m_{0,w}$) taking care to ensure that all air bubbles are remove (a detergent can be used). If the density of the material is less than 1 g/cm^3, it will be necessary to use a sink when weighing in water to ensure that the test pieces are completely immersed. If a sinker is used, determine th mass of the sinker alone in distilled water separately (mass m_s). Blot the test pieces dry with filter paper or a text fabric which does not deposit lint.

Immerse each test piece in the test liquid. At the end of the period of immersion, weigh each test piece in (mass m_i) to the nearest milligram, and then reweigh each test piece in distilled water (mass $m_{i,w}$) also at t standard laboratory temperature.

Calculate the percentage change in volume ΔV_{100} using the following equation:

$$\Delta V_{100} = \left(\frac{m_{\text{i}} - m_{\text{i,w}} + m_{\text{s,w}}}{m_0 - m_{0,\text{w}} + m_{\text{s,w}}} - 1 \right) \times 100 \qquad \text{...(2)}$$

where

m_0 is the initial mass of the test piece;

m_{i} is the mass of the test piece after immersion;

$m_{0,\text{w}}$ is the initial mass of the test piece in water (plus sinker if used);

$m_{\text{i,w}}$ is the mass of the test piece after immersion in water (plus sinker if used);

$m_{\text{s,w}}$ is the mass of the sinker in water, if used.

Report the result as the median value for the three test pieces.

If the test liquid is readily miscible with water or reacts with it, water cannot be used after immersion. If the test liquid is not too viscous or volatile at room temperature, a fresh portion of the test liquid can be used. If the test liquid is not suitable, use another liquid after immersion and calculate as follows:

$$\Delta V_{100} = \left[\frac{1}{\rho} \left(\frac{m_{\text{i}} - m_{\text{i,liq}} + m_{\text{s,liq}}}{m_0 - m_{0,\text{w}} + m_{\text{s,w}}} \right) - 1 \right] \times 100 \qquad \text{...(3)}$$

where

ρ is the density of the liquid;

$m_{\text{i,liq}}$ is the mass of the test piece (plus sinker, if used) in the liquid;

$m_{\text{s,liq}}$ is the mass of the sinker in the liquid, if used;

the other symbols are as defined for equation (2).

7.4 Change in dimensions

Measure the initial length of each test piece along its centre line to the nearest 0,5 mm at the standard laboratory temperature (taking measurements along the top and bottom surfaces and averaging the two results). Similarly measure the initial width by taking four measurements in all (top and bottom, both sides) near each end of the test piece.

Measure the initial thickness with the thickness gauge at four different points along the test piece and calculate the average of the results.

After immersion, re-measure the length, width and thickness of each test piece as described above.

Make all measurements with the test piece at the standard laboratory temperature.

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Calculate the percentage change in length Δl_{100} using the following equation:

$$\Delta l_{100} = \frac{l_i - l_0}{l_0} \times 100 \qquad \text{...(4)}$$

where

l_0 is the initial length;

l_i is the length after immersion.

Similarly, calculate the percentage changes in width and thickness.

Report the results as the median values for the three test pieces. The change in surface area can be calculated from the values obtained for the length and the width.

7.5 Change in surface area

Measure the initial lengths of the diagonals of each test piece to the nearest 0,01 mm at the standard laboratory temperature.

After immersion, re-measure the lengths of the diagonals as described above. If an optical measuring system is used, this may be done in a suitable glass container without removing the test pieces from the test liquid.

Calculate the percentage change in area ΔA_{100} using the following equation:

$$\Delta A_{100} = \left(\frac{l_A l_B}{l_a l_b} - 1 \right) \times 100 \qquad \text{...(5)}$$

where

l_a and l_b are the lengths of the diagonals before immersion;

l_A and l_B are the lengths of the diagonals after immersion.

If required, the percentage volume change ΔV_{100} may be calculated from the following equation:

$$\Delta V_{100} = \left[\left(\frac{l_A l_B}{l_a l_b} \right)^{3/2} - 1 \right] \times 100 \qquad \text{...(6)}$$

NOTE The equation for percentage volume change assumes isotropic swelling. If any doubt exists, determine the percentage volume change as specified in 7.3, which is the preferred method.

7.6 Change in hardness

Measure the IRHD hardness using the micro-test in accordance with ISO 48 on each test piece before and after immersion.

As an alternative, the normal IRHD hardness may be used with three plied-up test pieces, but in this case express the result as the apparent hardness.

Calculate the change in IRHD hardness ΔH, before and after immersion using the following equation:

$$\Delta H = H_i - H_0 \qquad \text{...(7)}$$

where

H_0 is the initial hardness;

H_i is the hardness after immersion.

7.7 Change in tensile stress-strain properties

Measure tensile stress-strain properties before and after immersion in accordance with ISO 37.

Calculate the tensile strength, the elongation at break and the stress at a given elongation using the initial cross-section of the test piece. Calculate the change in the property ΔX_{100} as a percentage of the value for unimmersed material using the following equation:

$$\Delta X_{100} = \frac{X_i - X_0}{X_0} \times 100 \qquad \text{...(8)}$$

where

X_0 is the initial value of the property;

X_i is the value of the property after immersion.

7.8 Test with liquid on one surface only

This test is applicable to relatively thin sheet materials, for example rubber diaphragms, which are exposed to liquid on one surface only during use.

Measure the nominal thickness of the test piece and then weigh it in air to the nearest milligram (mass m_0).

Then place the test piece in the apparatus as indicated in figure 1. Fill the chamber of the apparatus with the test liquid to a depth of approximately 15 mm and insert the plug (F). Maintain the apparatus at the required temperature for the duration of the test.

At the end of the contact period, bring the apparatus, if necessary, to the standard laboratory temperature. Remove the liquid and release the test piece. Remove any surplus liquid from the surface of the test piece by wiping with filter paper or a textile fabric which does not deposit lint. Then weigh the test piece to the nearest milligram (mass m_i) and measure the thickness at the standard laboratory temperature.

If the test liquid is volatile at room temperature, make the measurement within 2 min following removal from the liquid.

Express the change in mass per unit surface area Δm_A, in grams per square metre, using the following equation:

$$\Delta m_A = \frac{m_i - m_0}{A} \qquad \text{...(9)}$$

where

m_0 is the initial mass, in grams, of the test piece;

m_i is the final mass, in grams, of the test piece;

A is the area, in square metres, of the circular surface of the test piece in contact with the test liquid.

Report the result as the median for the three test pieces.

Calculate the change in thickness as specified in 7.4.

7.9 Determination of extractable matter

7.9.1 General

If the test liquid is readily volatile, the amount of matter which it extracts from the test piece can be determined either:

a) by drying the treated test piece and comparing its mass with the mass before immersion;

b) or by evaporating the test liquid to dryness and weighing the non-volatile residue.

Both methods are susceptible to error. In the method in which the dried test piece is weighed, the material can be oxidized if air is present during immersion; especially at high temperatures. In the method in which the test liquid is evaporated, there can be some loss of volatile extracted matter, especially plasticizers. Both methods are described in this International Standard and the choice between them depends on the nature of the material and the conditions of test.

It is difficult to define precisely what is meant by a "readily volatile" liquid, but it is suggested that the procedures described are not suitable for liquids less volatile than standard liquids A, B, C, D and E in annex A, i.e. for liquids boiling above 110 °C.

The determination of extractable matter shall be made after having determined the change in mass (7.2), the change in volume (7.3) and the change in dimensions (7.4).

7.9.2 By weighing the dried test piece

Dry the test piece, after immersion, under an absolute air pressure of approximately 20 kPa at approximately 40 °C to constant mass, i.e. until the difference between successive weighings at 30 min intervals does not exceed 1 mg.

The mass of extractable matter is taken as the difference between the original mass of the test piece and its mass after immersion and drying, expressed as a percentage of the original mass of the test piece.

7.9.3 By evaporating the test liquid

Transfer the liquid in which the test piece was immersed to a suitable container and wash the test piece with 25 ml of fresh liquid, and collect the washings in the same container. Evaporate the liquid and dry the residue to constant mass under an absolute air pressure of approximately 20 kPa at approximately 40 °C.

Carry out a blank test to estimate the solids content in a volume of the test liquid equal to that used for the immersion plus that used for washing.

The extractable matter content is taken as the mass of the dried residue, corrected for the result of the blank test, expressed as a percentage of the original mass of the test piece.

8 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) sample details:

   1) a full description of the sample and its origin,

   2) compound details, cure time and temperature where appropriate, time interval between vulcanization and testing,

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   3) the method of preparation of the test pieces from the sample, for example whether moulded or cut,

   4) a full description of the test liquid; in the case of mineral oils (other than reference oils 1, 2 and 3), this shall include the density, viscosity, refractive index and aniline point or aromatic content;

c) test method and test details:

   1) the method(s) used,

   2) the type of test piece used (dimensions),

   3) the standard laboratory temperature used,

   4) conditioning,

   5) the period and temperature of immersion;

   6) any deviation from the procedure specified;

d) test results:

   1) the results expressed in the form stated in the relevant clause,

   2) the appearance of the test piece (for example cracking, delamination) if appropriate,

   3) the appearance of the test liquid (for example discoloration, sedimentation) if appropriate;

e) the date of test.

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Annex A
(normative)

Reference liquids

WARNING — Appropriate safety precautions should be taken when preparing and handling test liquids, especially those known to be toxic, corrosive or flammable. Products giving off fumes should be handled only under an efficiently ventilated hood, corrosive products should not be allowed to come into contact with the skin or ordinary clothing, and flammable products should be kept away from any source of ignition.

A.1 Standard simulated fuels

Commercial fuels vary widely in composition even within the same grade (i.e. knock-rating) and from the same source. There are hydrocarbon-based fuels with and without oxygen compounds as well as alcohol-based fuels. The grade of gasoline is improved by aromatic or by oxygen-containing compounds, but these additives increase the effect of fuels on normally fuel-resistant rubbers. The composition varies with the situation on the gasoline market and with the geographical area and can change rapidly. Hence, several test liquids, which are used in practice, are recommended in tables A.1 and A.2 to cover the range of different compositions. They may also serve as guidelines for the formulation of other suitable test liquids. Analytical reagent quality materials shall be used in making up the test liquids. Test liquids containing alcohol shall not be used if the fuels involved are known to be free of alcohol.

Table A.1 — Standard simulated fuels without oxygen compounds

Liquid	Constituents	Content % (*V/V*)
A	2,2,4-trimethylpentane	100
B	2,2,4-trimethylpentane toluene	70 30
C	2,2,4-trimethylpentane toluene	50 50
D	2,2,4-trimethylpentane toluene	60 40
E	toluene	100
F	straight-chain paraffins (C_{12} to C_{18}) 1-methylnaphthalene	80 20

NOTE Liquids B, C and D simulate petroleum-derived fuels without oxygen compounds. Liquid F is intended to simulate diesel fuel, domestic heating oils and similar light furnace oils.

Table A.2 — Standard simulated fuels containing oxygen compounds (alcohols)

Liquid	Constituents	Content % (*V/V*)	
1	2,2,4-trimethylpentane	30	
	toluene	50	
	di-isobutylene	15	
	ethanol	5	
2	2,2,4-trimethylpentane	25,35	1)
	toluene	42,25	
	di-isobutylene	12,68	
	ethanol	4,22	
	methanol	15,00	
	water	0,50	
3	2,2,4-trimethylpentane	45	
	toluene	45	
	ethanol	7	
	methanol	3	
4	2,2,4-trimethylpentane	42,5	
	toluene	42,5	
	methanol	15	

1) This is equivalent to 84,5 % (*V/V*) of liquid 1 above.

A.2 Reference oils

A.2.1 General descriptions

A.2.1.1 Oil No. 1 (ASTM Oil No. 1)

This is a "low volume increase" oil consisting of a closely controlled blend of mineral oils comprising a solvent-extracted, chemically-treated dewaxed paraffinic residuum and neutral oil.

A.2.1.2 Oil No. 2 (IRM 902)

This is a "medium volume increase" oil obtained by solvent extraction and by acid and clay treatment of a high-viscosity distillate from selected naphthenic (Gulf Coastal) crude oils.

A.2.1.3 Oil No. 3 (IRM 903)

This is a "high volume increase" oil consisting of a closely controlled blend of two lubricating-oil fractions obtained by vacuum distillation of selected naphthenic (Gulf Coastal) crude oils.

A.2.1.4 Intended use

These reference oils are representative of low-additive mineral oils. Reference oils for high-additive or synthetic oils are in preparation.

A.2.2 Requirements

The oils shall contain no additives except, possibly, a trace (approximately 0,1 %) of a pour-point depressant, and shall have the properties specified in table A.3. The properties given in table A.4 are typical of the oils but cannot be guaranteed by suppliers.

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When these reference oils are required as test liquids, only those obtained from recognized suppliers shall be used for referee purposes and they shall be available for general use. However, in the event that they are not available, alternative oils can be used for routine testing only, provided that they comply with the requirements of table A.3 and also have been shown to give results similar to those obtained with the reference oils when testing rubbers of the same type of composition as those on which the routine tests are to be carried out.

Table A.3 — **Specifications of reference oils**

Property	Requirements			Method of test
	Oil No. 1	Oil No. 2	Oil No. 3	
Aniline point, °C	124 ± 1	93 ± 3	70 ± 1	ISO 2977
Kinematic viscosity, m^2/s (× 10^{-6})	20 ± 1 1)	20 ± 1 1)	33 ± 1 2)	ISO 3104
Flash point, °C min.	243	240	163	ISO 2592
Density, 15 °C, g/cm^3	0,886 ± 0,002	0,933 ± 0,006	0,921 ± 0,006	ISO 3675
Viscosity-gravity constant	—	0,865 ± 0,005	0,880± 0,005	
Naphthenics, C_N, %	—	⩾ 35	⩾ 40	
Paraffinics, C_P, %	—	⩽ 50	⩽ 45	

1) Measured at 99 °C.

2) Measured at 37,8 °C.

Table A.4 — **Typical properties of reference oils**

Property	Requirements			Method of test
	Oil No. 1	Oil No. 2	Oil No. 3	
Pour point, °C	—	– 12	– 31	ISO 3016
Refractive index at 20 °C	1,486 0	1,510 5	1,5026	ISO 5661
Aromatics, C_A, %	—	12	14	

NOTE Reference oils No. 1, 2 and 3 are identical to reference oils specified in ASTM D471-95, *Standard Test Method for Rubber Property — Effect of Liquids*, as ASTM Oil No. 1, IRM 902 and IRM 903, respectively. Reference oils IRM 902 and IRM 903 replace reference oils No. 2 and No. 3, respectively, from the former edition ASTM D471-91. These "old" oils were identical with the reference oils No. 2 and No. 3 in ISO 1817:1985. Oil No. 1 is unchanged.

Tables A.3 and A.4 give specifications and properties of the reference oils, but the critical parameter is the effect of the oils on physical properties of rubbers after immersion. Some tests have shown that the effect of "new" oils No. 2 and 3 can be less severe than the effect of "old" oils. Therefore, if specification testing is carried out with "old" reference oils No. 2 and 3, test programmes which make a direct comparison of the effect of "old" versus "new" reference oils on particular compounds and products are highly recommended.

A.3 Simulated service liquids

A.3.1 Liquid 101

Liquid 101 is intended to simulate synthetic diester-type lubricating oils. It is a blend comprising 99,5 % (*m/m*) of di-2-ethylhexyl sebacate and 0,5 % (*m/m*) of phenothiazine.

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A.3.2 Liquid 102

Liquid 102 is intended to simulate certain high-pressure hydraulic oils.

It is a blend comprising 95 % (*m/m*) of oil No. 1 and 5 % (*m/m*) of a hydrocarbon-compound oil additive containing 29,5 % (*m/m*) to 33 % (*m/m*) of sulfur, 1,5 % to 2 % (*m/m*) of phosphorus and 0,7 % (*m/m*) of nitrogen. A suitable additive is commercially available.

A.3.3 Liquid 103

Liquid 103 is intended to simulate phosphate-ester hydraulic oils used in aircraft. It is tri-*n*-butyl phosphate.

A.4 Chemical reagents

Tests with chemical reagents shall be carried out using the same chemicals at the same concentrations as those to be encountered in the intended use of the product. For general purposes, where no specification is known, the list of chemical reagents given in ISO 175 can be useful.