INTERNATIONAL STANDARD

ISO 10370

Second edition
2014-11-01

Petroleum products — Determination of carbon residue — Micro method

Produits pétroliers — Détermination du résidu de carbone — Méthode micro

Reference number
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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 28, *Petroleum products and lubricants*.

This second edition cancels and replaces the first edition (ISO 10370:1993). Apart from updates regarding reference fuels and chemicals, the results of an interlaboratory study carried out by the Energy Institute in the UK on the 10 % volume distillation residue procedure for middle distillates using 4 ml vials and automatic distillation units, have been incorporated. It also incorporates ISO 10370:1993/Cor1:1996.

Petroleum products — Determination of carbon residue — Micro method

WARNING — The use of this International Standard may involve hazardous materials, operations, and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a method for the determination of the amount of carbon residue, in the range 0,10 % (*m/m*) to 30,0 % (*m/m*), left after evaporation and pyrolysis of petroleum products under specified conditions.

NOTE 1 The carbon residue value serves as an approximation of the tendency of petroleum products to form carbonaceous deposits under similar degradation conditions, and may be useful in the assessment of relative carbon-forming tendencies of products within the same class. In this case, care should be taken in the interpretation of results.

For products which yield a residue in excess of 0,10 % (*m/m*), the test results are equivalent to those obtained by the Conradson carbon residue test (see ISO 6615[1]) in the range of 0,10 (*m/m*) to 25,0 (*m/m*) (for details see Annex A).

This International Standard is also applicable to petroleum products which consist essentially of distillate material, and which may yield a carbon residue below 0,10 % (*m/m*). On such materials, a 10 % (*V/V*) distillation residue is prepared by the procedure described in 7.3.1 and 7.3.2 before analysis.

Both ash-forming constituents, as defined by ISO 6245[2] and non-volatile additives present in the sample add to the carbon residue value and are included in the total value reported.

NOTE 2 The presence of organic nitrates incorporated in certain distillate fuels will yield abnormally high values for the carbon residue. The presence of alkyl nitrate in the fuel may be detected by ISO 13759.[3]

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

3 Terms and definitions

For the purposes of this document, the following term and definition apply

3.1
carbon residue
the whole residue produced of a sample from the specific conditions of evaporation and pyrolysis described in this International Standard

4 Principle

A weighed aliquot of the oil sample is placed in a glass vial and heated to 500 °C under an inert (nitrogen) gas stream in a controlled manner for a specific time. Volatiles formed during the reactions are swept away by the inert gas. The carbonaceous residue remaining is weighed.

5 Reagents and materials

5.1 Nitrogen, low oxygen content, i.e. 99,998 % (V/V) or better, with appropriate regulation to provide a delivery pressure of 0 kPa to 200 kPa.

NOTE The practical minimum delivery pressure is 140 kPa.

6 Apparatus

6.1 Glass sample vials, of 2 ml capacity, 12 mm outside diameter, approximately 35 mm high.

A vial of 4 ml capacity, 12 mm outside diameter, approximately 72 mm high may be used with samples of very low carbon residue content, i.e. below approximately 0,20 % (m/m), but no precision data has been obtained for them.

NOTE 1 An interlaboratory study[4] has been carried out by the Energy Institute on the 10 % volume distillation residue procedure for middle distillates using 4 ml vials and automatic distillation units and the precision is given in Clause 12.

NOTE 2 A glass sample vial of approximately 20 ml capacity (20,5 mm to 21 mm outside diameter by (70±1) mm high) for samples that are expected to yield residues < 0,10 % (m/m) may also be used, so that a more appreciable mass difference may be determined. In this case, a 5 g sample size is suggested. No precision has been determined for this technique, but it may be found suitable for very low 10 % residue samples.

6.2 Eyedropper or small rod, suitable for sample transfer.

6.3 Coking oven, comprising a circular heating chamber approximately 85 mm diameter by 100 mm deep for top-loading, capable of heating to 500 °C at a rate of between 10 °C and 40 °C per min, with exhaust port of 13 mm inside diameter for nitrogen purge of oven chamber (inlet near top, exhaust at bottom centre), with thermocouple sensor located in oven chamber next to but not touching sample vials, and with lid capable of sealing out air.

The condensate outlet leads into a short vertical section where most of the vapour condenses and falls into a removable trap located directly below the oven. A schematic diagram is given in Figure 1.

6.4 Sample vial holder, comprising a cylindrical aluminium block approximately 76 mm diameter by 17 mm thick with 12 evenly spaced holes (for vials) each 13 mm diameter by 13 mm deep.

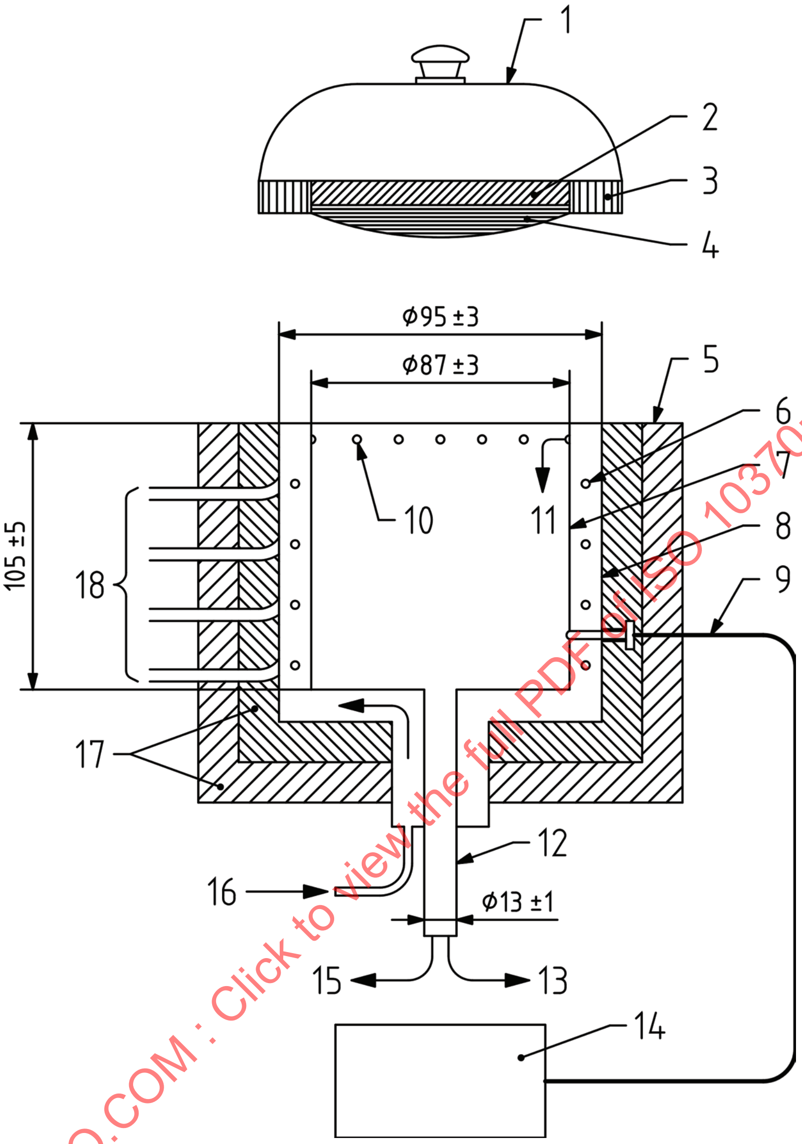
The holes shall be arranged in a circular pattern approximately 3 mm from the perimeter. The holder shall have legs 6 mm long with guides to centre in the oven chamber, and an index mark on the side to use as position reference. A typical holder is shown in Figure 2.

6.5 Thermocouple, iron-constantan, with exterior read-out and a range including 450 °C to 550 °C.

6.6 Analytical balance, of 0,1 mg sensitivity.

6.7 Cooling vessel, desiccator or similar tightly closed vessel, without desiccant.

Dimensions in millimetres

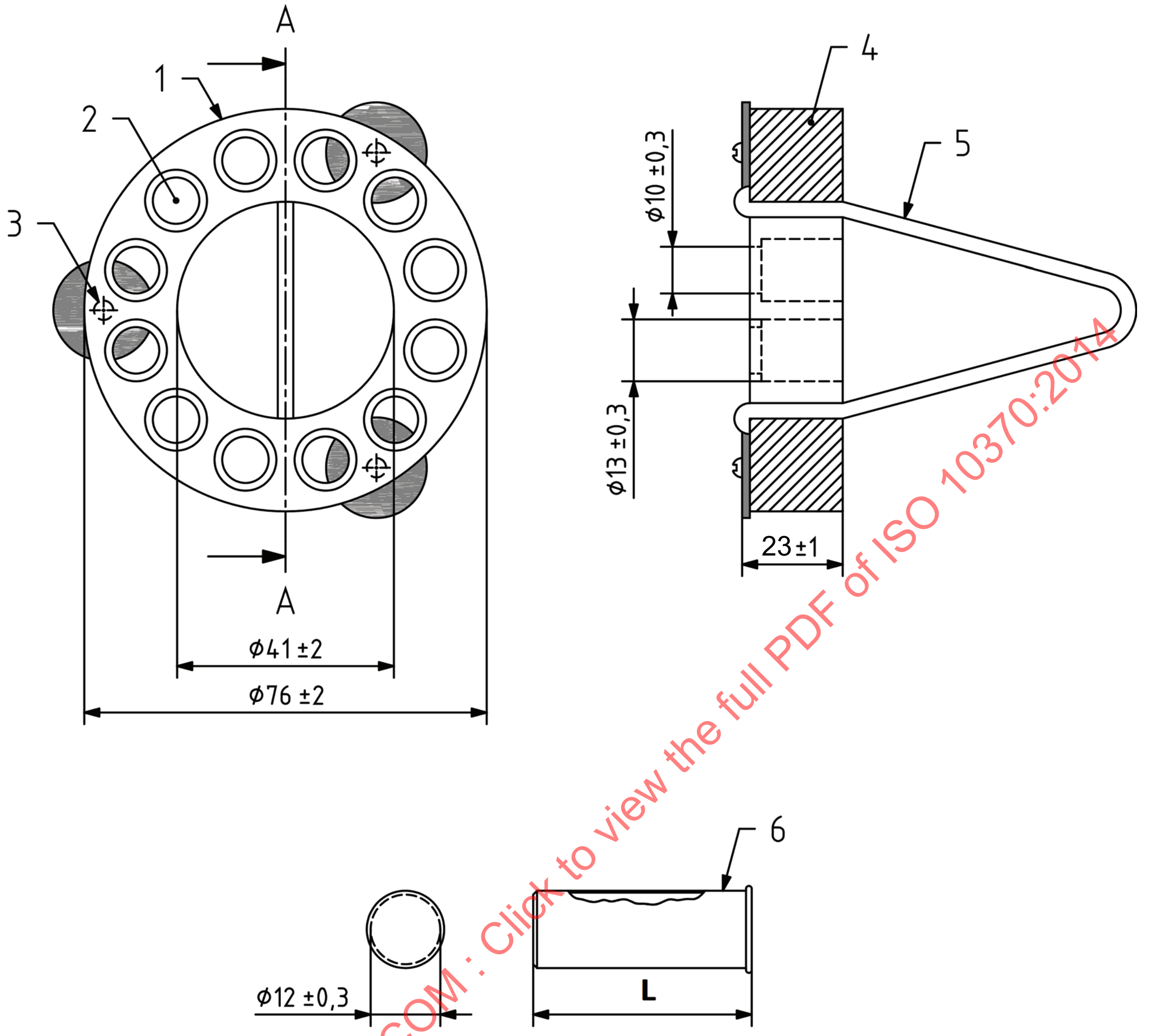


Key

1	lid
2	insulation
3	ceramic ring
4	304 stainless steel spherical top plug
5	oven
6	cross-section heater coils
7	inner cylindrical shell, stainless steel
8	outer cylindrical shell, stainless steel
9	thermocouple leads
10	series of holes (Ø 1)
11	nitrogen in
12	stainless steel exhaust tube
13	condensate
14	microprocessor control
15	smoke
16	nitrogen supply inlet
17	insulation (two layers)
18	heater lead to 2 × 700 W tubular heater coils

Figure 1 — Coking oven set-up

Dimensions in millimetres



Key

1	vial holder
2	12 identical holes uniformly spaced — vials fit loosely
3	small screws (three) for feet — steel basket centring washer (one on each foot)
4	ring — aluminium alloy material
5	handle — stainless steel alloy material
6	vial — soda lime glass
L	vial length — (37 ±3) for 2 ml and (72 ±3) for 4 ml

Figure 2 — Sample vial (soda lime glass, bottom) and vial holder (top)

7 Sample preparation

7.1 General instructions

For samples which consist essentially of distillate material, either follow the preparation as in 7.2 or prepare a distillation residue following a modified procedure of ISO 3405, given in 7.3. This latter procedure uses 4 ml vials (6.1) and shall be used for middle distillate samples which may yield a carbon residue below 0,30 % (*m*/*m*).

7.2 Regular procedure

Thoroughly stir the sample to be tested, first warming if necessary to reduce its viscosity. If the samples are in liquid form, transfer directly to the vials (6.1) using a rod or syringe. If the samples are solid materials, they shall either be heated, or frozen with liquid nitrogen and then shattered to provide manageable pieces.

7.3 Modified procedure

7.3.1 Ensure that the 4 ml vials (6.1) are clean and stored in a desiccator (without desiccant) before use. Set up the distillation as described in ISO 3405 using a clean 125 ml flask with no carbon deposits and add six glass or ceramic 'anti bumping' beads (1,5 mm to 2,5 mm diameter is recommended) to aid the mixing of residue as well as reducing bumping.

The thermometer may be omitted and replaced with a snug fitting, well rolled cork or silicone rubber stopper because it is the volume of distillate collected that is critical not the temperature of distillation. For an automatic unit, the temperature recording device may be necessary to allow the instrument to operate.

7.3.2 Discontinue heating when 88 ml of distillate has been recovered in the receiver. Allow the flask to cool for 5 min at the end of the distillation. Mix the residue in the flask by swirling. Immediately after mixing, transfer 2,5 ml to 3,0 ml to a pre-weighed vial of 4 ml (6.1) and reweigh. Take care to exclude any anti-bumping beads. This residue represents a 10 % (*V*/*V*) bottom portion of the original sample.

8 Sample transfer

8.1 During weighing and filling, handle the vials with forceps to minimize weighing errors. Discard the vials after use.

8.2 Weigh the clean sample vials, and record the mass to the nearest 0,1 mg.

8.3 Transfer an appropriate mass of the sample as indicated in Table 1 into the bottom of a weighed sample vial, taking care to avoid contact between the sample and the vial wall, reweigh to the nearest 0,1 mg and record. Place the loaded sample vials into the vial holder (up to 12), noting the position of each sample with respect to the index mark.

A control sample may be included in each batch of samples being tested. This control sample should be a typical sample which has been tested at least 20 times in the same equipment in order to define an average percent carbon residue and standard deviation.

Results for each batch are deemed acceptable when results for the control sample fall within the average percent carbon residue plus/minus three standard deviations. Control results which are outside these limits indicate problems with the procedure or the equipment.

Table 1 — Sample size

Sample description	Expected carbon residue % (*m*/*m*)	Sample size g
Black viscous or solid	> 5,0	0,15 ±0,05
Brown or black opaque and mobile	1,0 to 5,0	0,50 ±0,10
Transparent or translucent	0,2 to 1,0	1,50 ±0,50
Middle distillate, 10 % (*V*/*V*) residue	< 0,3	3,00 ±0,50 when used in conjunction with the 4 ml vial

9 Test procedure

9.1 With the oven at a temperature < 100 °C, place the vial holder, loaded as in 8.3, into the oven chamber and secure lid. Purge with nitrogen for at least 10 min at 600 ml/min. Subsequently, decrease the purge to 150 ml/min and heat the oven slowly to 500 °C at a rate of 10 °C/min to 15 °C/min.

9.2 Hold the oven at 500 °C ±2 °C for 15 min. Then shut off furnace power and allow the oven to cool freely while under a nitrogen purge of 600 ml/min. When the oven temperature is < 250 °C, remove the vial holder for further cooling in the desiccator.

NOTE 1 After the samples are removed from the oven, the nitrogen purge may be shut off.

If the sample foams or spatters causing loss of sample, discard and repeat the test.

NOTE 2 Spattering may be due to water that may be re-moved by prior gentle heating under reduced pressure, followed by a nitrogen sweep. Alternatively, a smaller size may be used.

If another test is to be run, remove the lid to allow faster cooling.

NOTE 3 A subsequent test may be started when the oven has cooled to below 100 °C.

WARNING — Do not open the oven to air at any time during the heating cycle, as the introduction of air (oxygen) may form an explosive mixture with the volatile coking products formed. Do not open the oven until the oven temperature has fallen to below 250 °C during the cooling step. Maintain the nitrogen flow until after the vial holder has been removed from the oven.

Either locate the coking oven in a laboratory exhaust hood for safe venting of smoke and fumes, or install a vent line from the oven exhaust to the laboratory exhaust system, being careful not to create negative pressure in the line.

9.3 Handling the vials with forceps, transfer them to the desiccator and allow them to cool to room temperature.

Weigh each cooled vial to the nearest 0,1 mg and record its mass.

Discard the used glass sample vials.

9.4 Examine the condensate trap at the bottom of the oven chamber; empty if necessary and replace.

WARNING — The condensate trap residue may contain some carcinogenic materials, and contact with them should be avoided. They should be properly disposed of according to acceptable procedures.

10 Calculation

Calculate the mass percentage of carbon residue in the original sample, or in the 10 % (*V*/*V*) distillation residue, to the nearest 0,01 % (*m*/*m*), μ_{CR}, using the following formula:

$$\mu_{CR} = \frac{m_3 - m_1}{m_2 - m_1} \times 100 \qquad (1)$$

where

m_1 is the mass of the empty vial, in grams;

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

m_3 is the mass of vial + residue, in grams.

For the relationship of carbon residue by micro method (this International Standard) to carbon residue by Conradson method (see ISO 6615[1]), Annex A may be used.

11 Expression of results

Report results obtained from Formula (1) as "Carbon residue — micro method" to the nearest 0,01 % (*m*/*m*).

Or report carbon residue micro method on 10 % (*V*/*V*) residue to the nearest 0,01 % (*m*/*m*).

12 Precision

12.1 General

The precision given was derived from statistical analysis by ISO 4259[5] of the results of interlaboratory testing of a matrix of fuels and were first published in 1983. The precision is shown graphically in Figure 3.

The precision data for 10 % volume residue come from statistical examination of the results of interlaboratory testing according to ISO 4259 of a matrix of fuels including automotive diesel fuels, gasoils, fuels containing up to 10 % (*V*/*V*) of fatty acid methyl esters (FAME), fuels with cetane improver and marine fuel, which was carried out by the Energy Institute in 2007.

12.2 Repeatability, *r*

The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of the test method, exceed the values given in Formula (2), only in one case in 20:

$$r = 0{,}077\,0\,X^{2/3} \qquad (2)$$

where

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

For carbon residue-micro method on 10 % volume distillation residue, using 4 ml vials, the repeatability is.

$$r = 0{,}143\,0\,X^{0{,}5} \qquad (3)$$

12.3 Reproducibility, *R*

The difference between two test results independently obtained by different operators operating in different laboratories on identical test material would, in the normal and correct operation of the test method, exceed the values given in Formula (4) only in one case in 20:

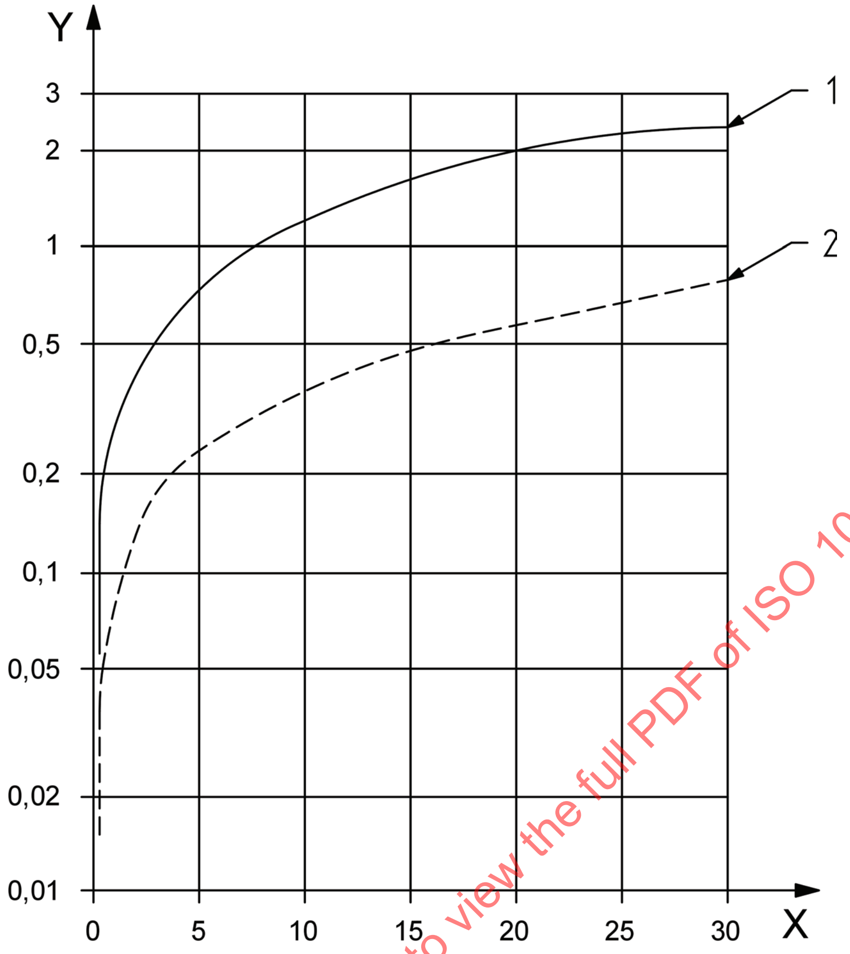
$$R = 0{,}245\,1\,X^{2/3} \qquad (4)$$

where

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

For carbon residue-micro method on 10 % volume distillation residue, using 4 ml vials, the reproducibility is:

$$R= 0{,}212\,5\,X^{0{,}5} \qquad (5)$$



Key

X-axis carbon residue — micro method average in % (*m*/*m*)

Y-axis carbon residue — micro method difference in % (*m*/*m*)

1 reproducibility, *R*

2 repeatability, *r*

Figure 3 — Carbon residue — Micro method — Precision data

13 Test report

The test report shall contain at least the following information:

a) type and complete identification of the product tested;

b) a reference to this International Standard (i.e. ISO 10370);

c) results of the test (see Clause 11);

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

e) date of the test.