
**Petroleum products and lubricants —
Inhibited mineral turbine oils —
Determination of oxidation stability**

*Produits pétroliers et lubrifiants — Huiles minérales inhibées pour
turbines — Détermination de la stabilité à l'oxydation*



Foreword

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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 7624 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Annexes A, B and C form an integral part of this International Standard.

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Petroleum products and lubricants — Inhibited mineral turbine oils — Determination of oxidation stability

WARNING — The use of this International Standard may involve hazardous material, 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 resistance to oxidation under specified conditions of unused inhibited mineral turbine oils. The method is also applicable to other types of oil, such as hydraulic oil.

NOTE — This method may be used for specification purposes, and is of value in estimating the oxidation stability of turbine lubricants in the laboratory. It should be recognized, however, that correlation between the results of any single method of test for oxidation stability and the stability of an oil in service will vary with service conditions.

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 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*.

3 Principle

Oxygen is passed for 164 h through a sample of the oil with added soluble metal catalysts (iron and copper) and maintained at 120 °C. The volatile acid products, the acidity of the oil, and the sludge formed are determined. If it is required to measure the length of time to obtain a pronounced increase in the rate of evolution of volatile acids (induction period), an acidity/time curve is obtained by daily determinations of the volatile acids.

4 Reagents and materials

During the analyses, use only reagents of recognized analytical grade and water meeting the requirements of ISO 3696 Grade 2 or water of equivalent purity, unless otherwise specified.

4.1 Catalysts

Prepare 1 % (*m/m*) solutions of copper naphthenate and iron naphthenate by dilution of master solutions which conform to annex A. After dilution, the solutions shall have a total trace metals content (other than sodium) of not greater than 300 mg/kg. Use mineral oil containing approximately 5 % aromatic carbon as the diluent for the working solutions. Store this solution in the dark.

NOTE — High boiling turbine base oil of ISO VG 32 viscosity is recommended.

Do not use white paraffinic oils because of the lower solubility of the iron naphthenate.

4.2 Oxygen, commercial product (minimum purity 99,4 %).

The oxygen shall be dried by passing through a suitable desiccant. The oxygen delivery system shall be constructed such that a smooth flow of oxygen is delivered to the measuring device. At the beginning of each test-run, the oxygen flow-rate given by the measuring device, shall be set to 1,0 l/h \pm 0,1 l/h and checked with the soap bubble flowmeter (5.6), and from there on, when carrying out daily flow checks, the rate shall be maintained at 1,0 l/h \pm 0,1 l/h for the duration of the test, and checked by the soap bubble meter if considered necessary.

WARNING — Use only with equipment conditioned for oxygen service by careful cleaning to remove oil, grease and other combustibles. Do not use oils or grease on regulators, gauges or control equipment. If a leak in the oxygen supply pipework is suspected, turn off immediately and seek qualified assistance. Depressurize the pipework prior to investigating a leak. The oxygen supply system should be checked regularly.

4.3 Alkali blue, 20 g/l solution in ethanol (4.10).

To obtain a good end-point with alkali blue indicator, after dissolving in ethanol (4.10), add 0,03 ml of HCl (4.6) to each 1 ml of indicator solution. After 24 h, carry out a check acid value determination to ensure that sensitization has occurred, i.e. a distinct colour change from a blue to a red which is comparable to that of a 10 % solution of cobalt nitrate [Co(NO₃)₂·6H₂O].

4.4 Phenolphthalein, 10 g/l alcoholic indicator solution.

4.5 Heptane, analytical grade, or of equal or greater purity.

4.6 Hydrochloric acid, aqueous solution of 0,1 mol/l HCl.

4.7 Potassium hydroxide, standard volumetric ethanolic solution of $c_{\text{KOH}} = 0,1$ mol/l. Standardize daily or as appropriate.

4.8 Toluene.

4.9 Dichloromethane. Dispose of waste dichloromethane in an approved manner.

4.10 Ethanol, denatured, containing approximately 5 % (V/V) water.

4.11 Sulfuric acid, concentrated, 98 % (*m/m*) minimum H₂SO₄.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Oxidation tubes, borosilicate or neutral glass conforming to the dimensions shown in figure 1.

Dimensions in millimetres

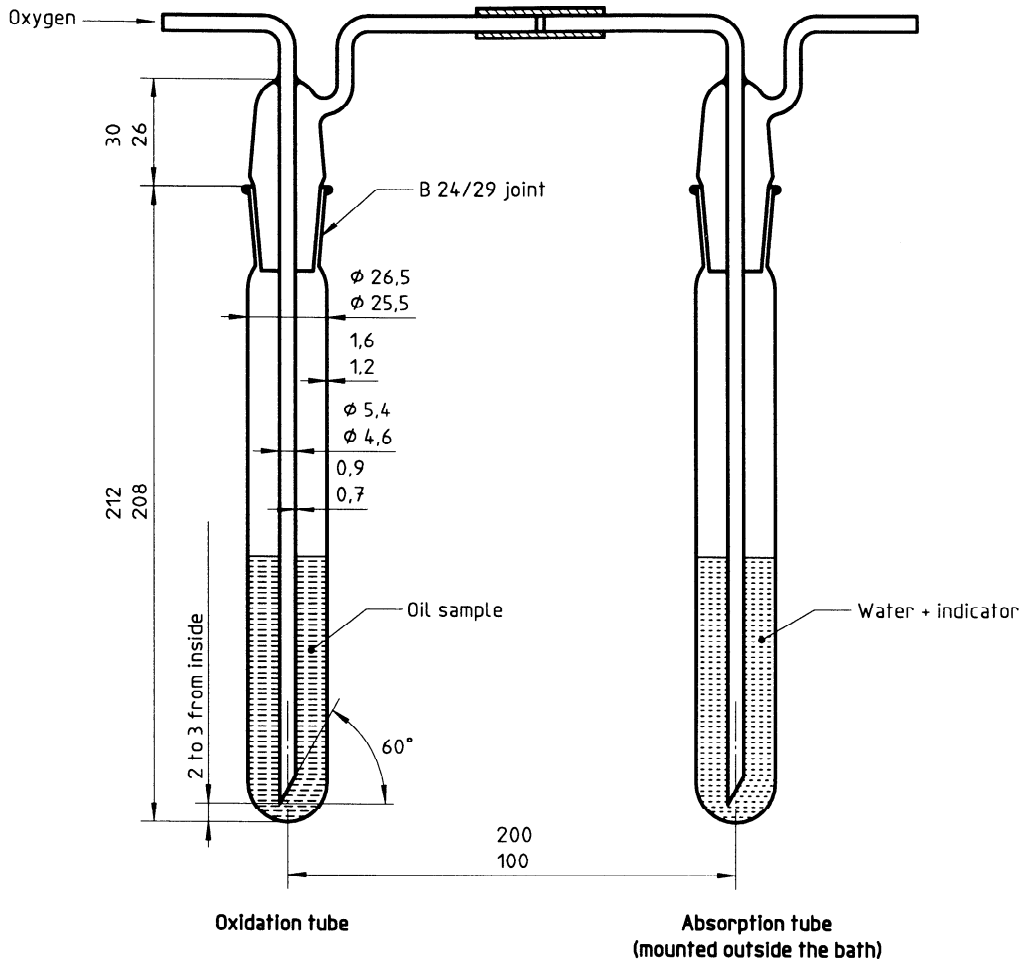


Figure 1 — Oxidation and absorption tubes

5.2 Absorption tubes, identical to the oxidation tubes (5.1).

The connection between oxidation and absorption tubes shall be as short as possible and made by means of short flexible silicone rubber sleeves (length between axis of the two tubes 150 mm ± 50 mm). These tubes shall be mounted outside the bath.

5.3 Heating bath, aluminium alloy block heater or oil bath thermostatically controlled to maintain the oil in the desired number of oxidation tubes at a temperature of 120 °C ± 0,5 °C (see figure 2).

Read the temperature from a type B thermometer or a temperature measuring device (5.8), inserted in a test tube to within 5 mm from the bottom. Fill the test tube up to the immersion line of the thermometer with the oil under test, and place in the heating bath.

The temperature of the upper surface shall be kept at 60 °C ± 5 °C (see note) and measured using a type A thermometer or a temperature measuring device (5.8) (see figure 2). The surfaces of the block, other than that against the upper surface of the heating bath, shall be protected by suitable insulation. This block shall be placed as near to the holes as practicable and within the area of the aluminium heater block.

NOTE — 60 °C ± 5 °C applies for an ambient temperature of 20 °C, which should be used for assessing equipment compliance. Operation outside 60 °C ± 5 °C due to extremes of ambient temperature has only a slight effect on test results.

Dimensions in millimetres

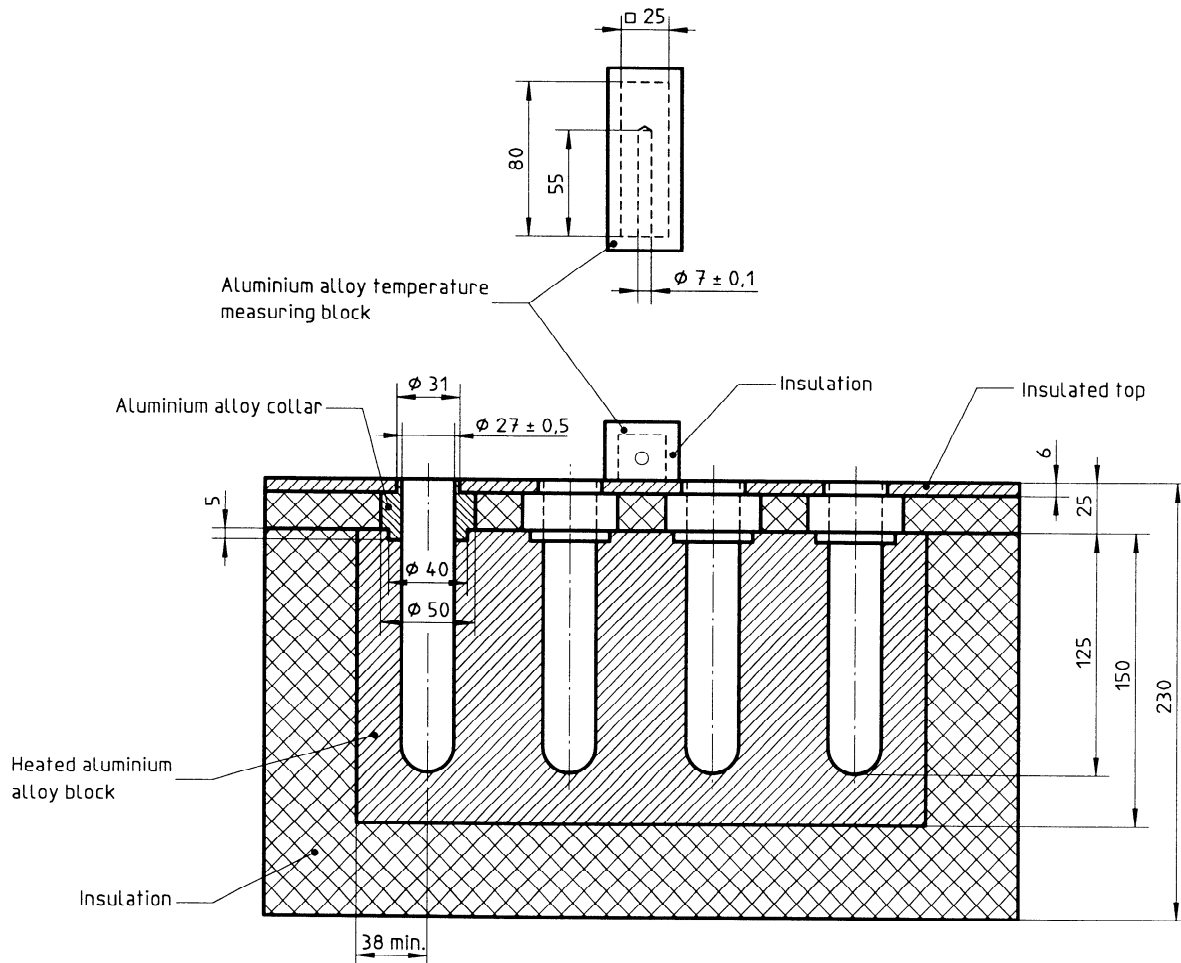


Figure 2 — Typical metal heating bath

When an aluminium block heater is used, the test tubes shall be inserted into the holes to an overall depth of 150 mm. The depth of the holes in the heating part of the block shall be at least 125 mm and short metal collars, passing through the insulating cover and surrounding each oxidation tube, ensure heating over the 150 mm length of the tube.

If an oil bath is used, the oxidation tubes shall be immersed to a depth of 137 mm in the oil and to an overall depth of 150 mm in the bath.

For both types of heating bath, the height of the oxidation tubes above the upper surface shall be 60 mm and the diameter of the holes shall be just sufficient to allow insertion of the specified tube. In case of slackness, place a 25 mm diameter O-ring about the tube and press it against the heater surface.

5.4 Membrane filters, 5 µm porosity, 47 mm diameter, compatible with the fluid under test.

5.5 Evaporating dish, 50 ml capacity.

5.6 Soap bubble flowmeter, for checking the oxygen flow rate. See figure 3 for a typical assembly.

5.7 Burette, readable to 0,01 ml or better.

5.8 Thermometers, conforming to specifications given in annex B, or temperature measuring devices of suitable range and of equal or greater accuracy.

Dimensions in millimetres

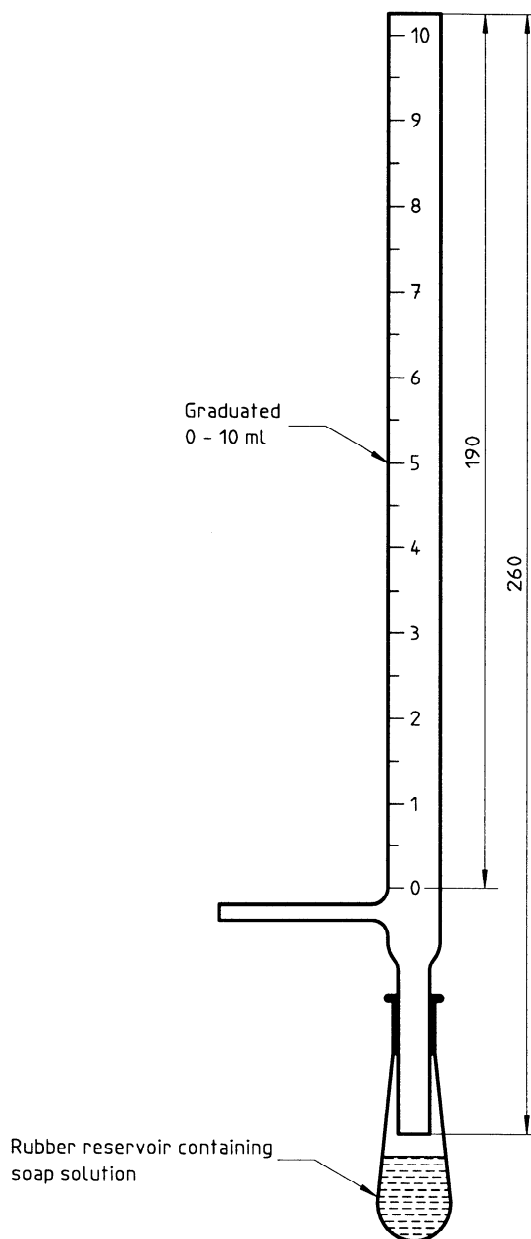


Figure 3 — Soap bubble flowmeter

5.9 Air oven, capable of being controlled at $75\text{ °C} \pm 5\text{ °C}$ and $110\text{ °C} \pm 5\text{ °C}$.

5.10 Filtration apparatus, for use with the membrane filters (5.4) with a minimum capacity of 1 litre.

5.11 Conical flask, 500 ml capacity, fitted with a ground glass stopper.

6 Procedure

6.1 Preparation of apparatus

Chemically clean the oxidation and absorption tubes.

NOTE — A satisfactory method of cleaning is to wash with acetone, followed by water.

Drain and then soak in concentrated sulfuric acid (4.11) for a minimum of 16 h. Drain and completely remove the acid by washing, first with tap water, then with water (see clause 4). Dry the tubes in the oven (5.9) at $110\text{ °C} \pm 5\text{ °C}$ for at least 3 h, and then allow them to cool to room temperature.

6.2 Oxidation

6.2.1 Weigh quantities of copper naphthenate and iron naphthenate solutions (4.1) necessary to obtain copper and iron concentrations in the oil under test of $20\text{ mg/kg} \pm 0,5\text{ mg/kg}$ [$60\text{ mg} \pm 0,4\text{ mg}$ for 1,0 (*m/m*) solutions] into a suitable size of beaker or flask. Weigh $30\text{ g} \pm 0,04\text{ g}$ of the oil under test into the beaker or flask containing the copper and iron naphthenates.

6.2.2 Heat the sample gently for a maximum of 5 min to a maximum of 80 °C . After dissolution of the catalysts, cool and weigh $25\text{ g} \pm 0,04\text{ g}$ of the sample into an oxidation tube (5.1). Place the oxidation tube in the heating bath (5.3), maintained at $120\text{ °C} \pm 0,5\text{ °C}$. Use a drop of the sample under test to seal the ground-glass joint of the test vessel.

6.2.3 Connect the oxidation tube to the oxygen supply (4.2) and to an absorption tube (5.2) containing 25 ml of water and 5 or 6 drops of the phenolphthalein indicator solution (4.4).

To avoid evaporation of water, protect the absorption tube from the heating bath by insulation.

6.2.4 Adjust the flow of oxygen to $1\text{ l/h} \pm 0,1\text{ l/h}$, and check it daily. Maintain the temperature at $120\text{ °C} \pm 0,5\text{ °C}$ during the 164 h test period.

6.2.5 If determination of the induction period is required, after 24 h disconnect the absorbing vessel containing water and indicator. Titrate the volatile acids collected with ethanolic potassium hydroxide solution (4.7), record the amount of titrant used and calculate the volatile acids content. Reconnect the absorption vessel containing the neutralized water. Repeat this procedure every 24 h up to a total of 164 h. Plot an acidity/time curve. If more data points are required, carry out two determinations with starting times separated by 6 h.

6.2.6 If determination of the induction period is not required, after 164 h, stop the oxygen flow, disconnect the oxidation and absorption tubes and remove the oxidation tube from the heating bath.

6.3 Determination of volatile acids content

As quickly as possible after the test, titrate the water in the absorption tube with the ethanolic potassium hydroxide solution (4.7).

6.4 Determination of sludge content

6.4.1 In cases of dispute or for refereeing purposes, determine the sludge content in accordance with annex C. For routine testing, determine the sludge content in accordance with 6.4.2 to 6.4.6.

6.4.2 Cool the sample of artificially aged oil in the dark for 1 h and then pour it into a conical flask (5.11). Use 300 ml of heptane (4.5) to recover the sample adhering to the test tube and oxygen lead-in tube and add the washings to the sample in the flask.

6.4.3 Allow the mixture to stand in the dark for a minimum of 16 h, at room temperature, then filter through a membrane filter (5.4), previously dried at 80 °C for 1 h and weighed to $\pm 0,1\text{ mg}$. Re-filter any cloudy filtrates through the same filter.

6.4.4 Carefully remove all traces of sample by repeated washing of the sludge with heptane (4.5), using a total volume of 150 ml of heptane.

6.4.5 With the vacuum applied, carefully remove the clamp and funnel. Wash the periphery of the filter with a small volume of heptane (4.5) by directing it in a gently stream from the edge towards the centre, taking care not to wash any of the sludge from the surface of the filter. Maintain the vacuum after the final wash only for the few seconds necessary to remove excess heptane. Retain the filtrate and washings for soluble acidity determinations (6.5). Carefully remove the filter, dry at $75\text{ °C} \pm 5\text{ °C}$ for 1 h, and weigh to $\pm 0,1\text{ mg}$.

6.4.6 Dissolve any sludge adhering to the test tube and to the oxygen lead-in tube in small quantities of dichloromethane (4.9) using a total of 30 ml, and transfer the solution into a tared porcelain crucible. After the evaporation of the dichloromethane, dry for 1 h in the oven (5.9), maintained at $110\text{ °C} \pm 5\text{ °C}$. Cool and weigh to $\pm 0,1\text{ mg}$.

6.5 Determination of soluble acidity

6.5.1 Collect the heptane solution obtained after filtering off the sludge (see 6.4) in a 500 ml measuring flask and make up to the mark with heptane (4.5). Carry out three determinations of the acid value on either 100 ml aliquots of the heptane/oil solution, or if testing very dark oils, use a smaller volume to enable the end-point to be seen. Record the volume of heptane/oil solution used as V_3 .

NOTE — A single determination of acidity is normally adequate, but three determinations should be made for refereeing purposes.

6.5.2 Immediately before use, prepare the titration solvent by adding 2 ml of alkali blue solution (4.3) to 100 ml of a mixture of 60 ml of toluene (4.8) and 40 ml of ethanol (4.10). Neutralize the mixture with ethanolic potassium hydroxide solution (4.7) to give a red colour comparable to that of a 10 % (*m/m*) solution of cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] that persists for at least 15 s. Add this neutralized solvent, with swirling, to either 100 ml of heptane/oil solution, or if testing very dark oils, use a smaller volume to enable the end-point to be seen. Titrate with potassium hydroxide ethanolic solution at a temperature not exceeding 30 °C . Correct the soluble acidity for the reduced volume of heptane/oil used.

7 Calculation

7.1 Volatile acidity

Calculate the volatile acidity, VA, in grams of potassium hydroxide per kilogram, using the following equation.

$$VA = \frac{56,1 V_1 c}{25}$$

where

- 56,1 is the relative molar mass, in grams per mole, of potassium hydroxide;
- V_1 is the volume, in millilitres, of ethanolic potassium hydroxide solution, used for titration of the water in the absorption tube (see 6.2);
- c is the concentration, in moles per litre, of the ethanolic potassium hydroxide solution.

7.2 Total sludge

Calculate the total sludge content, TS, as a percentage by mass, using the following equation.

$$TS = 4(m_1 + m_2)$$

where

- m_1 is the mass, in grams, of the sludge insoluble in heptane;
- m_2 is the mass, in grams, of the sludge recovered by dichloromethane.

7.3 Soluble acidity

Calculate the soluble acidity, SA, in grams of potassium hydroxide per kilogram, using the following equation.

$$SA = \frac{56,1 V_2 c}{5} \times \frac{100}{V_3}$$

where

V_2 is the volume, in millilitres, of potassium hydroxide ethanolic solution required to neutralize the heptane/oil solution (see 6.5);

V_3 is the volume, in millilitres, of heptane/oil solution used in 6.5.1;

c is the concentration, in moles per litre, of the potassium hydroxide ethanolic solution.

7.4 Total oxidation

Calculate the total oxidation products content, TOP, as a percentage by mass, using the following equation.

$$TOP = TS + \left[\frac{180(SA + VA)}{561} \right]$$

where

180 is the average relative molecular mass, in grams per mole, of the oxidized acids;

561 is 10 times 56,1, the relative molar mass, in grams per mole, of potassium hydroxide.

8 Expression of results

Express the results as the total oxidation product, TOP, to the nearest 0,01 %. Express the ratio of sludge to TOP, TS/TOP, to the nearest whole number.

9 Precision

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, in the normal and correct operation of the test method, would exceed the values shown in table 1 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 nominally identical test material, in the normal and correct operation of the test method, would exceed the values shown in table 1 only in one case in twenty.

Table 1 — Precision values

	Repeatability	Reproducibility
Total acidity	$0,228X^{0,8}$	$0,747X^{0,8}$
Total sludge, %	$0,283X^{0,666}$	$0,821X^{0,666}$
Total oxidation products (TOP), %	$0,192X$	$0,685X$

where X is the mean of the two results being compared.

NOTE — Precision is given for typical values of X in tables 2, 3 and 4.

These precision values were obtained from tests on oils giving results in the range 0,5 to 11 total acidity, 0,03 % to 3,0 % sludge and 0,25 % to 5,70 % TOP.

Table 2 — Typical precision values for total acidity

Mean result, X	Repeatability	Reproducibility
0,5	0,13	0,43
1,0	0,22	0,74
2,0	0,40	1,30
4,0	0,69	2,26
6,0	0,95	3,13
8,0	1,20	3,94
10,0	1,43	4,71

Table 3 — Typical precision values for total sludge % (m/m)

Mean result, X	Repeatability	Reproducibility
0,05	0,04	0,11
0,1	0,06	0,17
0,2	0,09	0,28
0,5	0,17	0,51
1,0	0,28	0,82
2,0	0,45	1,30
3,0	0,58	1,70

Table 4 — Typical precision values for total oxidation products (TOP) % (m/m)

Mean result, X	Repeatability	Reproducibility
0,25	0,04	0,17
0,50	0,09	0,34
1,00	0,19	0,68
2,00	0,38	1,37
4,00	0,76	2,74
5,70	1,09	3,90

10 Test report

The test report shall contain at least the following information:

- a reference to this International Standard;
- the type and identification of the product tested;
- the result of the test (see clause 8);
- any deviation, by agreement or otherwise, from the procedure specified;
- the date of the test.

Annex A (normative)

Iron naphthenate and copper naphthenate master solutions

The master solution of iron naphthenate shall contain a minimum of 5,0 (m/m) iron and have an impurity content not exceeding that given in table A.1.

Table A.1 — Iron naphthenate master solution

Impurity	Maximum mg/kg
Copper	2
Manganese	50
Zinc	10
Alkaline and alkaline earth metals other than sodium	100
Chlorine	1
Phosphates	2

The master solution of copper naphthenate shall contain a minimum of 5,0 % (m/m) copper and have an impurity content not exceeding that given in table A.2.

Table A.2 — Copper naphthenate master solution

Impurity	Maximum mg/kg
Iron	20
Nickel	4
Zinc	30
Alkaline and alkaline earth metals other than sodium	100
Chloride	1

Annex B (normative)

Thermometer specifications

		Type A	Type B
Temperature range	°C	– 5 to 110	98 to 152
Immersion	mm	57	100
Graduations			
subdivisions	°C	0,5	0,2
long lines at each	°C	1 and 5	1
numbers at each	°C	5	2
Scale errors, maximum	°C	0,5	0,3
Expansion chamber permit heating to	°C	160	180
Total length	mm	290 ± 5	395 ± 5
Stem outer diameter	mm	$6,5 \pm 0,5$	7 ± 1
Bulb length	mm	11 ± 2	$17,5 \pm 2,5$
Bulb outside diameter	mm	$\leq 5,5$ and \geq stem	\geq stem
Scale location			
bottom of bulb to line at	°C	0	98
distance	mm	90 ± 5	135 ± 10
Length of graduated portion	mm	140 to 175	190 to 235
Stem enlargement			
outside diameter	mm	$8,0 \pm 0,5$	—
length	mm	2,5 to 5,0	—
distance to bottom	mm	65 ± 1	—
Contraction chamber			
distance to top, maximum	mm	—	35 ¹⁾

1) Mercury shall be near the bottom of the chamber at 0 °C.

NOTE — IP 15C/ASTM 9C thermometers meet the requirements given for type A and IP 81C/ASTM 41C thermometers meet the requirements given for type B.

Annex C (normative)

Alternative procedure for sludge determination

C.1 Scope

This annex specifies an alternative procedure to that given in 6.4 for determining the sludge content of the oil/heptane mixture. The procedure given in this annex shall be used in cases of dispute or for refereeing purposes.

C.2 Apparatus

Use the apparatus given in clause 5 except membrane filters (5.4).

C.2.1 Filter crucibles, with sintered glass of porosity grade P10 as specified in ISO 4793.

C.3 Procedure

C.3.1 Cool the sample of artificially aged oil in the dark for 1 h and then pour it into a conical flask (5.11). Use 300 ml of the heptane (4.5) to recover the sample adhering to the test tube and oxygen lead-in tube and add the washings to the oil in the flask.

C.3.2 Allow the mixture to stand in the dark for a minimum of 16 h, at room temperature, then filter through a filter crucible (C.2.1) previously dried at 100 °C for 1 h, and weighed to $\pm 0,1$ mg. Re-filter any cloudy filtrates.

C.3.3 Carefully remove all traces of oil by repeated washing of the sludge with heptane (4.5). Use a total volume of 150 ml of the heptane for the washing of the sludge. Retain the filtrate and washings in order to determine the soluble acidity (see 6.5).

Dry the filter crucible in an oven (5.9) at $110 \text{ °C} \pm 5 \text{ °C}$ for 1 h, and weigh to $\pm 0,1$ mg.

C.3.4 Dissolve any sludge adhering to the test tube and to the oxygen lead-in tube in small quantities of dichloromethane (4.9) using a total of 30 ml, and transfer the solution into a tared porcelain crucible. After the evaporation of the dichloromethane, dry for 1 h in the oven (5.9), maintained at $110 \text{ °C} \pm 5 \text{ °C}$. Cool and weigh to $\pm 0,1$ mg.

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