

INTERNATIONAL STANDARD

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Petroleum products — Determination of the oxidation stability of middle-distillate fuels

*Produits pétroliers — Détermination de la stabilité à l'oxydation des
distillats moyens de pétrole*



Reference number
ISO 12205:1995(E)

Foreword

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International Standard ISO 12205 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

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Petroleum products — Determination of the oxidation stability of middle-distillate fuels

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

1 Scope

This International Standard describes a procedure for the measurement of inherent stability of middle-distillate petroleum fuels under accelerated oxidizing conditions. It is not applicable to fuels containing residual components, or any significant component from a non-petroleum source.

The method provides a basis for the estimation of the storage stability, under the conditions of this test, of middle-distillate fuels with an initial boiling point above approximately 175 °C and a 90% (V/V) recovery point below 370 °C.

The method may not provide a prediction of the quantity of insolubles that will form in field storage over any given period of time. The amount of such insolubles is subject to the specific conditions, which are too variable for this test method to predict accurately.

NOTE 1 Oxidation is a chemical process causing adherent and filterable insolubles to form. Any substance such as copper or chromium that catalyses oxidation reactions will cause greater quantities of insolubles to form.

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

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

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

ISO 6246:—¹⁾, *Petroleum products — Gum content of light and middle distillate fuels — Jet evaporation method*.

ISO 6353-2:1983 and Addendum 2:1986, *Reagents for chemical analysis — Part 2: Specifications — First series*.

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 adherent insolubles: Material, produced in the course of stressing middle-distillate fuel under the conditions of this test, that adheres to the glassware after the fuel has been flushed from the system.

1) To be published. (Revision of ISO 6246:1981)

3.2 filterable insolubles: Material, produced in the course of stressing middle-distillate fuel under the conditions of this test, that is capable of being removed from the fuel by filtration. This includes both material suspended in the fuel and material removed easily from the oxidation cell and oxygen delivery tube with hydrocarbon solvent.

3.3 inherent stability: Resistance to change when exposed to air, but in the absence of other environmental factors such as water, or reactive metallic surfaces or dirt.

3.4 total insolubles: Sum of adherent and filterable insolubles.

3.5 zero time: Time at which the first oxidation cell is placed in the heating bath.

4 Principle

A test portion of filtered middle-distillate fuel is aged at 95 °C for 16 h while bubbling oxygen through the sample. After ageing, the sample is cooled to approximately room temperature before filtering to obtain the quantity of filterable insolubles. Adherent insolubles are then removed from the oxidation cell and associated glassware with trisolvent. The trisolvent is evaporated to obtain the quantity of adherent insolubles. The sum of the filterable and adherent insolubles is reported as total insolubles.

5 Reagents and materials

Reagent grade solvents, conforming to the requirements of ISO 6353 or better, shall be used for the preparation of the trisolvent (TAM). Water shall conform to grade 3 of ISO 3696.

NOTE 2 It has been found that commercial grades of solvents, if used for the procedures of this International Standard, can have levels of impurities that will affect the result.

5.1 Acetone, CH_3COCH_3 .

5.2 Toluene, $\text{C}_6\text{H}_5\text{CH}_3$.

5.3 Methanol, CH_3OH .

5.4 Trisolvent (TAM), comprising a solution of equal volumes of acetone (5.1), toluene (5.2) and methanol (5.3).

5.5 2,2,4-trimethylpentane (iso-octane), $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$, of minimum purity 99,5 %.

5.6 Oxygen, minimum purity 99,5 %.

When oxygen is delivered through a plant system of piping, a filter shall be provided adjacent to the heating bath (6.2). Control the oxygen supply by an appropriate regulation system.

6 Apparatus

All measuring apparatus shall be calibrated, verified and periodically monitored for performance, as appropriate and according to manufacturer's instructions, to assure consistency of results.

6.1 Oxidation cell, of borosilicate glass as shown in figure 1, consisting of a test tube, condenser and oxygen delivery tube.

Since the apparatus used in this test can also be used in ISO 4263 (see annex A), where coils of copper and steel are used, ensure that any residue that could contain these metals is eliminated from the apparatus by thorough cleaning prior to use.

To preclude the presence of chromium ions, as well as to protect laboratory personnel from potential harm, chromosulfuric acid shall not be used for cleaning glassware in the practice of this method.

6.2 Heating bath, containing a liquid medium whose temperature is thermostatically controlled to maintain the fuel in the oxidation cells at a temperature of $95,0\text{ }^\circ\text{C} \pm 0,2\text{ }^\circ\text{C}$ (see note 4).

It shall be fitted with a suitable stirring device to provide a uniform temperature throughout the bath, and large enough to hold the desired number of oxidation cells immersed to a depth of approximately 350 mm. Further, the bath construction shall shield the fuel samples from light while they are undergoing oxidation. A minimum liquid capacity of 6 l per oxidation cell shall be provided.

NOTES

3 It has been found that a bath temperature in the range of $95,5\text{ }^\circ\text{C}$ to $95,8\text{ }^\circ\text{C}$ is necessary to maintain the fuel temperature in the specified range.

4 A metal block bath, conforming to the same capacity and control requirements, is also suitable.

Dimensions in millimetres

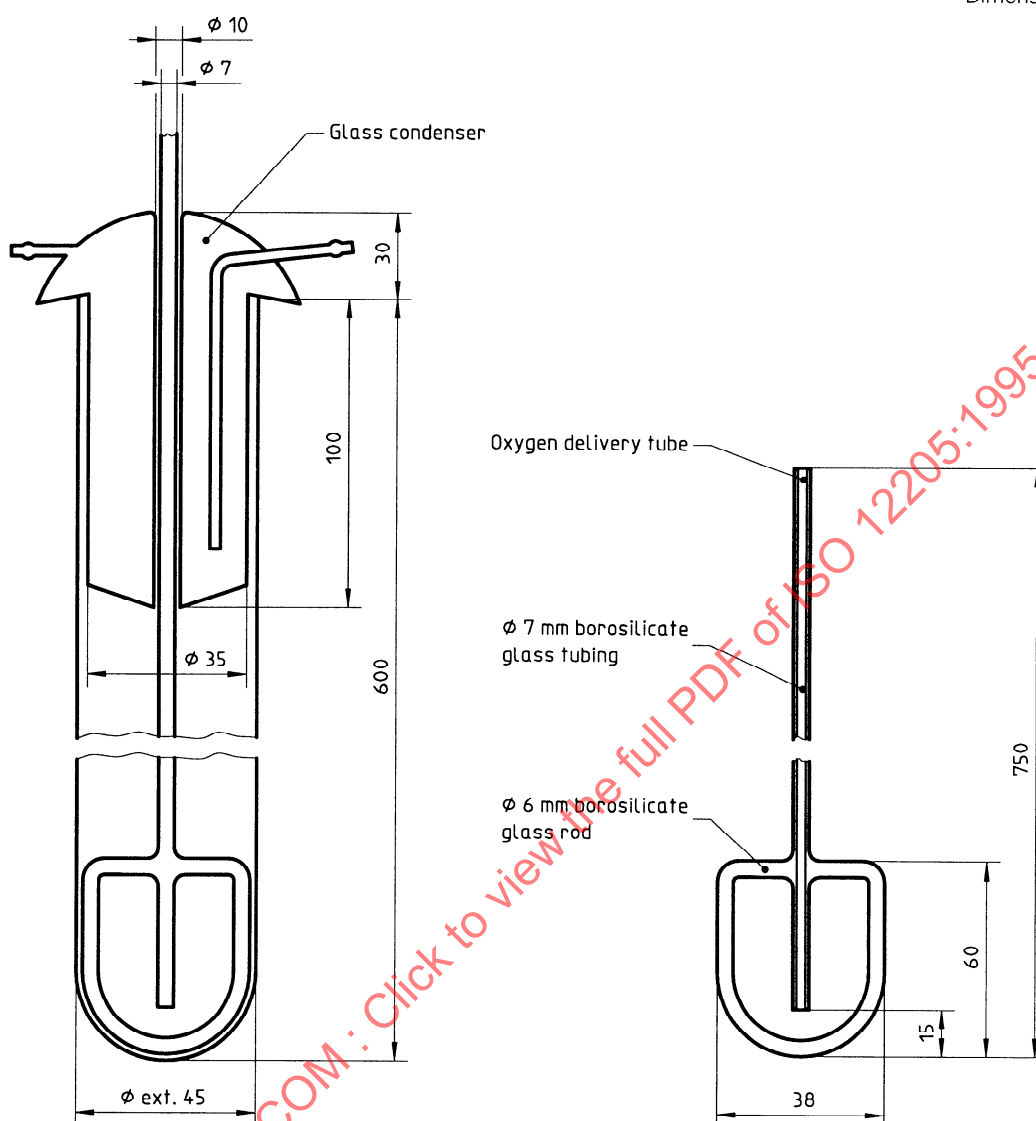


Figure 1 — Oxidation cell

6.3 Flowmeters, capable of measuring 3,0 l/h $\pm$ 0,3 l/h of oxygen flow. One flowmeter shall be provided for each oxidation cell.

6.4 Filter drying oven, capable of safely evaporating the solvent at $80\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ for the drying of filter materials.

6.5 Glassware drying oven, capable of drying glassware at $105\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$.

6.6 Filter assembly, capable of holding the filter media (6.7), as illustrated in figure 2.

6.7 Filter media, 47 mm diameter, of nylon membrane with a nominal pore diameter of $0,8\text{ }\mu\text{m}$.

Use single filters for prefiltration, and matched pairs for the determination of filterable insolubles.

NOTE 5 Whilst the use of nylon membrane filters is preferred, as they have advantages with regard to handling, cellulose ester membrane filters may also be used.

6.8 Evaporating vessels, comprising tall form beakers of borosilicate glass, of capacity either 200 ml or 100 ml depending on the technique, for determining adherent insolubles (10.5).

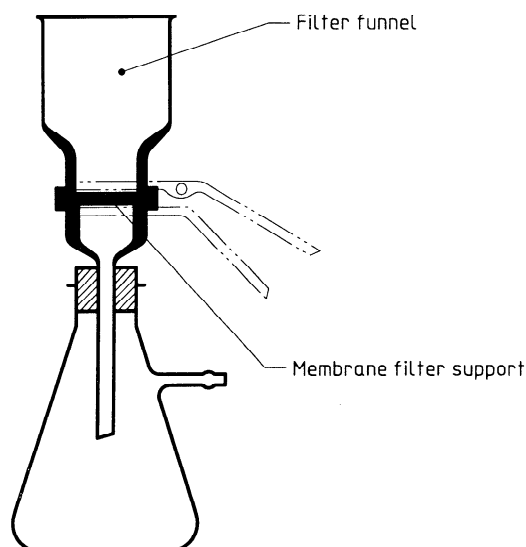


Figure 2 — Filter assembly

6.9 General apparatus

A balance capable of weighing to 0,1 mg, a hotplate capable of heating the liquid in the evaporating vessels (6.8) to 135 °C, a desiccator (without desiccant), spade-ended forceps for handling the filter media, and a suitable timing device.

7 Apparatus preparation

7.1 Preparation of glassware other than oxidation cells

Rinse all glassware thoroughly with trisolvent (5.4) followed by water, then wash with a mildly alkaline or neutral laboratory detergent. Rinse three times with grade 3 water (5) followed by acetone (5.1) to remove water, and allow to dry.

7.2 Preparation of oxidation cells and accessories

After completion of 7.1, fill oxidation cells with laboratory detergent in grade 3 water (5). Place the oxygen delivery tube in the oxidation cell, place the condenser over the oxygen delivery tube, and allow to soak for at least 2 h. Wash, drain, then rinse five times with tap water followed by three rinses with grade 3 water (5). Rinse with acetone (5.1), drain, and allow the oxidation cell and delivery tube to dry.

7.3 Preparation of evaporating beakers

Dry the cleaned evaporating vessels (6.8) for 60 min in the oven (6.5). Place the beakers in the desiccator (6.9), and allow to cool for 60 min. Weigh the beakers to the nearest 0,1 mg.

8 Sampling

8.1 Samples shall be taken by the procedure described in ISO 3170, ISO 3171 or an equivalent national standard.

8.2 Test portions from the samples shall be drawn after thorough mixing and subdivision away from direct sunlight, and in an area that would be compatible with other laboratory operations. Storage before stress, the stress period and cool-down after stressing shall occur in the dark.

8.3 Containers for samples shall be of metal lined with epoxy resin or similar material, previously rinsed twice with the material to be sampled, or borosilicate glass, if they are wrapped or boxed to exclude light. Do not use soft (soda) glass containers, or plastic containers (due to the potential for leaching of plasticizers).

8.4 Analyse fuel samples as soon as possible after receipt.

NOTE 6 If a fuel cannot be tested within one day, it should be blanketed with an inert gas such as oxygen-free nitrogen, argon or helium, and stored at a temperature no higher than 10 °C, but not lower than its cloud point.

9 Sample preparation

9.1 If the received sample is in a tank, drum or container exceeding 19 l capacity, use the subdivision procedures described in 8.2.

9.2 Thoroughly mix smaller samples by shaking, rolling or other techniques before taking a laboratory sample by pouring, pipetting or other means.

9.3 Clean any tube, thief, pipette, beaker or other apparatus or equipment that is to come into contact with the received sample, with trisolvent (5.4) followed by a portion of the sample prior to use. Allow samples that have been stored at temperatures significantly below 10 °C to warm to room temperature, and examine for the absence of any undissolved wax prior to mixing thoroughly and taking an aliquot.

NOTE 7 Warming allows any separated wax to redissolve, and the viscosity to decrease to a point at which mixing is effective. Agitation during the warming period assists the redissolution of the wax.

10 Procedure

10.1 Sample filtration

Place a single filter membrane (6.7) on the filter support, and clamp the filter funnel to the support as shown in figure 2. Apply suction of approximately 80 kPa (an absolute pressure of approximately 20 kPa in the flask). Pour 400 ml of the fuel through the filter (6.7) into a clean (7.1) 500 ml glass suction flask. After filtration is complete, discard the filter medium. Repeat preparation for each sample to be run.

Never use the same filters for a second increment of fuel, because any material deposited on the filters by a previous increment of fuel can result in a greater removal of solids from the next increment.

10.2 Assembling the oxidation apparatus

Place a clean oxygen delivery tube into a clean oxidation cell (7.2), and pour $350 \text{ ml} \pm 5 \text{ ml}$ of the filtered fuel into the cell. As soon thereafter as possible, but never more than 60 min after measuring the fuel, immerse the test cell in the heating bath (6.2) such that the level of fuel in the oxidation cell shall be below the level of the liquid medium in the heating bath. *During any interim period, store the cell in the dark.*

Place a condenser over the oxygen delivery tube and oxidation cell; connect the condenser to the cooling water. Connect the oxygen delivery tube to the oxygen supply through the flowmeter, and adjust the oxygen flow to $3,0 \text{ l/h} \pm 0,3 \text{ l/h}$. Ensure samples are protected from light.

Record the time the first oxidation cell is placed in the bath as zero time, and allow the cell to remain in the bath for $16,00 \text{ h} \pm 0,25 \text{ h}$. Note the sequence of placement of oxidation cells in the bath.

When the number of test cells is less than the capacity of the heating bath, the bath shall be filled with oxidation cells containing 350 ml of a stable liquid. No oxygen delivery tube or condenser is required for these "dummy" tubes.

10.3 Cooling the sample

Remove the sample(s) from the heating bath in the same sequence as they were placed therein, cover the opening of each cell with a piece of aluminium foil

or plastic to prevent entrance of dirt or dust. Record the time of removal as an interval from zero time. Place the cell(s) in a dark ventilated site at room temperature, which shall be above the cloud point of the fuel. Leave the samples until they have attained room temperature, but for no longer than 4 h.

10.4 Determining filterable insolubles

Assemble the filter apparatus as illustrated in figure 2, using one pair of matched mass filters (6.7). Apply suction (approximately 80 kPa), and pour the cooled sample through the filter. Pull all the fuel through the filter before *completely* rinsing the oxidation cell and oxygen delivery tube with three separate $50 \text{ ml} \pm 5 \text{ ml}$ volumes of 2,2,4-trimethylpentane (5.5). Pass all rinsings through the filter assembly. After filtration is complete, disconnect the top part of the filter assembly and wash down the rim of the filter-media-adjacent parts of the filter assembly with a further $50 \text{ ml} \pm 5 \text{ ml}$ of 2,2,4-trimethylpentane. Discard the filtrate. Dry the two filter media at 80°C for 30 min, cool them for 30 min, and weigh the upper (sample) and lower (blank) filters separately to the nearest 0,1 mg.

NOTE 8 Using matched mass filters assumes no collection of sediment on the lower filter medium that has passed through the upper medium, and that the blank correction is for sample/solvent absorption. Occasionally, material is retained on the lower filter after having passed through the upper medium. If there is a visible deposit, or if the mass gain of the lower filter exceeds 10 mg, the sum of the mass gains should be used for the calculations.

If severe filter plugging occurs, and filtration cannot be completed within 120 min, filter the remaining fuel through a separate set of weighed filters, using a further $50 \text{ ml} \pm 5 \text{ ml}$ portion of 2,2,4-trimethylpentane to wash down the filter media and filter assembly.

10.5 Determining adherent insolubles

After completing the rinsing of the oxidation cell and oxygen delivery tube as described in 10.4, dissolve the adherent insolubles from them using three equal rinses of trisolvent (5.4) totalling $75 \text{ ml} \pm 5 \text{ ml}$. The oxidation cell and oxygen delivery tube shall be examined for evidence of stain or colour, indicating incomplete removal. If such stain or colour is noted, rinse with a fourth 25 ml volume of trisolvent.

Either collect the rinsings in one or more tared 100 ml beakers (6.8) as specified in ISO 6246 and evaporate the trisolvent mixture at 160°C by the air jet procedure described in ISO 6246, or alternatively, collect the rinsings in a tared 200 ml beaker (6.8) and evaporate the trisolvent mixture with extreme caution

(especially if carrying out the procedure on more than one beaker at a time) by placing on the 135 °C hotplate (6.9) located under a hood.

When all the solvent has been evaporated, place the tared beaker(s) containing adherent insolubles in the desiccator (6.9) to cool for 60 min. An adherent insolubles blank, to correct for the presence of impurities in the solvents, shall be run on a volume of trisolvant (5.4) equal to that used in the test. When dry and cool, weigh the beakers to the nearest 0,1 mg.

11 Calculation

11.1 Filterable insolubles

Calculate the filterable insolubles, *A*, in grams per cubic metre, using the following equation:

$$A = \frac{m_2 - m_1}{0,35}$$

where

*m*₁ is the mass of the blank (bottom) filter, in milligrams;

*m*₂ is the mass of the sample (top) filter, in milligrams.

11.2 Adherent insolubles

Calculate the adherent insolubles, *B*, in grams per cubic metre, using the following equation:

$$B = \frac{(m_6 - m_4) - (m_5 - m_3)}{0,35}$$

where

*m*₃ is the tare mass of the blank beaker, in milligrams;

*m*₄ is the tare mass of the sample beaker, in milligrams;

*m*₅ is the final mass of the blank beaker, in milligrams;

*m*₆ is the final mass of the sample beaker, in milligrams.

11.3 Total insolubles

Calculate the total insolubles, *C*, in grams per cubic metre, using the following equation:

$$C = A + B$$

NOTE 9 Some specifications may still use the historical units of milligrams per 100 ml. In this instance, the results above should be divided by 10; or 3,5 should be used as the divisor in the equations in 11.1 and 11.2.

12 Expression of results

12.1 Report the total insolubles (*C*) to the nearest 1 g/m³, and the number of filters used (10.4).

Optionally, also report the filterable insolubles (*A*) and the adherent insolubles (*B*), to the nearest 1 g/m³.

12.2 Report the time that the oxidation cell was in the heating bath, if other than 16 h ± 0,25 h.

13 Precision

Some examples of calculated precision values at several levels of total insolubles are given in table 1.

NOTE 10 The same precision values apply if either of the two optional methods are used for the determination of adherent insolubles.

13.1 Repeatability, *r*

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of the test method, exceed the value below only in one case in 20:

$$r = 5,4 \left(\frac{C}{10} \right)^{0,25}$$

where *C* is the average value of the total insolubles being compared, in grams per cubic metre.

13.2 Reproducibility, *R*

The difference between two test results independently obtained by different operators operating in different laboratories on nominally identical test material would, in the normal and correct operation of the test method, exceed the value below only in one case in 20:

$$R = 10,6 \left(\frac{C}{10} \right)^{0,25}$$

where *C* is the average value of the total insolubles being compared, in grams per cubic metre.

Table 1 — Calculated precision data

Total insolubles	Repeatability,	Reproducibility,
g/m^3	r g/m^3	R g/m^3
15	6,0	11,7
20	6,4	12,6
25	6,8	13,3
30	7,1	14,0

14 Test report

The test report shall contain at least the following information:

- sufficient details for complete identification of the product tested;
- a reference to this International Standard;
- the results of the test (see clause 12);
- any deviation, by agreement or otherwise, from the procedure specified;
- the date of the test.

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