INTERNATIONAL STANDARD

ISO 7537

Second edition
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Petroleum products — Determination of acid number — Semi-micro colour-indicator titration method

Produits pétroliers — Détermination de l'indice d'acide — Méthode de titrage semi-micro par indicateur coloré

Reference number
ISO 7537:1997(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 7537 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This second edition cancels and replaces the first edition (ISO 7537:1989), which has been technically revised.

Annex A of this International Standard is for information only.

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Petroleum products — Determination of acid number — Semi-micro colour-indicator titration 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 semi-micro colour-indicator method for the determination of acidic constituents in new or used petroleum products and lubricants soluble in mixtures of toluene and propan-2-ol, or capable of existing as suspensions in such mixtures, and where the suspended material is sufficiently dissociated that its acidic components can be titrated.

The method is especially intended for applications in which the amount of sample available to be analysed is too small to allow accurate analysis by ISO 6619 or ISO 6618. It is applicable to the determination of acids having dissociation constants in water larger than 10^{-9}. Extremely weak acids having dissociation constants smaller than 10^{-9} do not interfere. Salts titrate if their hydrolysis constants are larger than 10^{-9}.

NOTE 1 This method may be used to indicate relative changes in acid number that occur in an oil during use under oxidizing conditions. Although the titration is made under definite equilibrium conditions, the method does not measure an absolute acidic property that can be used to predict performance of an oil under service conditions. No general relationship between bearing corrosion and acid number is known.

NOTE 2 Since this test method requires substantially less sample than ISO 6618 or ISO 6619, it provides an advantageous means of monitoring an oxidation test by changes in acid number by:

a) minimizing test sample depletion for acid number analyses and thus minimizing the disturbance of the test, and

b) allowing additional acid number analyses to be made while maintaining the same test sample depletion, and thus providing additional data.

NOTE 3 Some oils, such as many cutting oils, rustproofing oils, and similar compounded oils, or excessively dark-coloured oils, may be more difficult to analyse by this method due to obscurity of the colour-indicator end-point. These oils can be analyzed by ISO 6619 provided sufficient sample is available. However, this situation is much less likely using this International Standard than using ISO 6618, since the sample is more dilute during the titration and the end-point colour change is more stable. The acid numbers obtained by this method may or may not be numerically the same as those obtained by ISO 6619, but they should be of the same order of magnitude.

NOTE 4 The results obtained using this method have been found to be numerically the same as those obtained using ISO 6618, within the precision of the two methods, for new or oxidized lubricants of the type primarily intended for hydraulic or steam turbine type service. The oxidized lubricants were obtained using ISO 4263.

This correlation is shown by the correlation coefficient $r = 0{,}989$ with slope $s = 1{,}017$ and intercept $y = +0{,}029$, calculated using the acid numbers obtained using both titration methods for the samples used for the precision statement (see clause 11).

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 listed 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 6353-2:1983, *Reagents for chemical analysis — Part 2: Specifications — First series.*

ISO 6618:1997, *Petroleum products and lubricants — Determination of acid and base number — Colour-indicator titration method.*

3 Definition

For the purposes of this International Standard, the following definition applies:

3.1 acid number: The quantity of potassium hydroxide (KOH), expressed in milligrams, required to titrate acids or salts present in one gram of sample to a specified end-point, when the dissociation or hydrolysis constants are larger than 10^{-9}.

4 Principle

The sample is dissolved in a toluene/propan-2-ol solvent containing a small amount of water, and the resulting single-phase solution is titrated at room temperature with standard alcoholic potassium hydroxide solution under a nitrogen atmosphere. The end-point is the stable green colour of the added *p*-naphtholbenzein indicator.

5 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognised analytical grade. All references to water shall be understood to mean freshly distilled (carbon dioxide free) water conforming to grade 3 of ISO 3696.

NOTE 5 For the purposes of this International Standard, the term "% (*V*/*V*)" is used to represent the volume fraction of a material.

5.1 ***p*-Naphtholbenzein indicator solution**, conforming to the specifications given in annexes A and B of ISO 6618:1997. Prepare a solution containing 10 g of *p*-naphtholbenzein per litre of titration solvent.

NOTE 6 In a study in 1992, only one commercially available source of this indicator met the specification now given in annex A of ISO 6618:1997. Careful adherence to this requirement is therefore required.

5.2 Nitrogen, of minimum purity 99,5 %, dry and carbon dioxide free.

NOTE 7 In order to obtain repeatable results and a stable end-point colour change, it is especially important that the nitrogen purge gas be free of carbon dioxide. Prepurified grade nitrogen has been found to be satisfactory.

5.3 Phenolphthalein indicator solution.

5.3.1 Preparation

Dissolve 0,10 g of pure, solid phenolphthalein in 50 ml of water and 50 ml of 95 % (*V*/*V*) ethanol.

5.4 Propan-2-ol, anhydrous, with a maximum water content of 0,90 % (V/V).

5.5 Toluene, conforming to the requirements of ISO 6353-2.

5.6 Titration solvent. Add 500 ml ± 2 ml of toluene (5.5) and 5 ml ± 0,1 ml of water to 495 ml ± 2 ml of propan-2-ol (5.4).

5.7 Potassium hydroxide, alcoholic solution, standard volumetric c(KOH) = 0,01 mol/l. Use commercially available solution, or prepare in accordance with 5.7.1 and standardize in accordance with 5.7.2.

5.7.1 Preparation

Add 3 g of solid KOH to approximately 1 l of propan-2-ol (5.4) in a 2 l conical flask. Boil the mixture gently on a steam bath for 15 min while stirring to prevent caking of solids on the bottom of the flask.

Add approximately 1 g of barium hydroxide and again boil gently for approximately 10 min.

Cool to room temperature, stopper to prevent contact with the ambient atmosphere, and allow to stand overnight (16 h).

Filter the supernatant liquid through a 10 µm polytetrafluorethylene (PTFE) membrane filter while avoiding unnecessary exposure to the atmosphere, and then dilute the solution (approximately 0,05 mol/l) with propan-2-ol (5.4) to a total volume of approximately 5 l, to obtain a final concentration of 0,010 mol/l ± 0,002 mol/l.

NOTE 8 Smaller volumes than 5 l may be required for laboratories performing this test less frequently. Quantities and glassware sizes may be scaled down proportionately.

Store the titrant in a chemically resistant dispensing bottle out of contact with cork, rubber or saponifiable stopcock lubricant, and protected by a guard tube containing soda-lime. Minimize exposure of the titrant to light by storing in the dark or in an amber bottle or by wrapping the bottle with aluminium foil.

NOTE 9 Because of the relatively large coefficient of cubic expansion of organic liquids such as propan-2-ol, the standard alcoholic solutions should be standardized at temperatures close to those employed in the titrations of samples.

5.7.2 Standardization

Standardize the titrant against 0,05 g ± 0,01 g of pure potassium phthalate ($KHC_8H_4O_4$), dried (at least 1 h at 110 °C) using the method specified in 8.1 for the acid number analysis, but using water (40 ml ± 1 ml) as the solvent and 6 drops of phenolphthalein as the indicator. Titrate to a pink colour that endures for 5 s ± 1 s.

Carry out the blank in the same manner, but omitting the potassium hydrogen phthalate, taking care to titrate to a similar colour change. Standardize the titrant frequently enough to detect variations exceeding 0,000 3 mol/l.

Calculate the concentration of potassium hydroxide, c_{KOH}, in mol/l, using the following equation:

$$c_{\mathrm{KOH}} = \frac{1\,000\, m_1}{204{,}2\,(V_1 - V_2)}$$

where

m_1 is the mass, in grams, of potassium hydrogen phthalate titrated;

V_1 is the volume, in millilitres, used for the potassium hydrogen phthalate titration;

V_2 is the volume, in millilitres, used for the blank titration.

Take the mean concentration determined by at least duplicate analyses as the titrant concentration for the acid number calculations.

6 Apparatus

6.1 Titration burette, micro scale, automatic, with 0,01 ml subdivisions and at least 2 ml burette capacity.

6.2 Titrant reservoir, preferably integral with the burette (see figure 1). If a separate reservoir is used, the line connecting the reservoir with the burette shall be all glass.

The reservoir shall be of amber glass or shall be wrapped in opaque material (e.g. aluminium foil) to minimize exposure of the titrant to light.

To ensure that precipitate collects undisturbed, the tube in the reservoir for titrant withdrawal shall be adjusted so that the end of the tube is approximately 20 mm from the bottom of the reservoir, and movement of the reservoir shall be minimized.

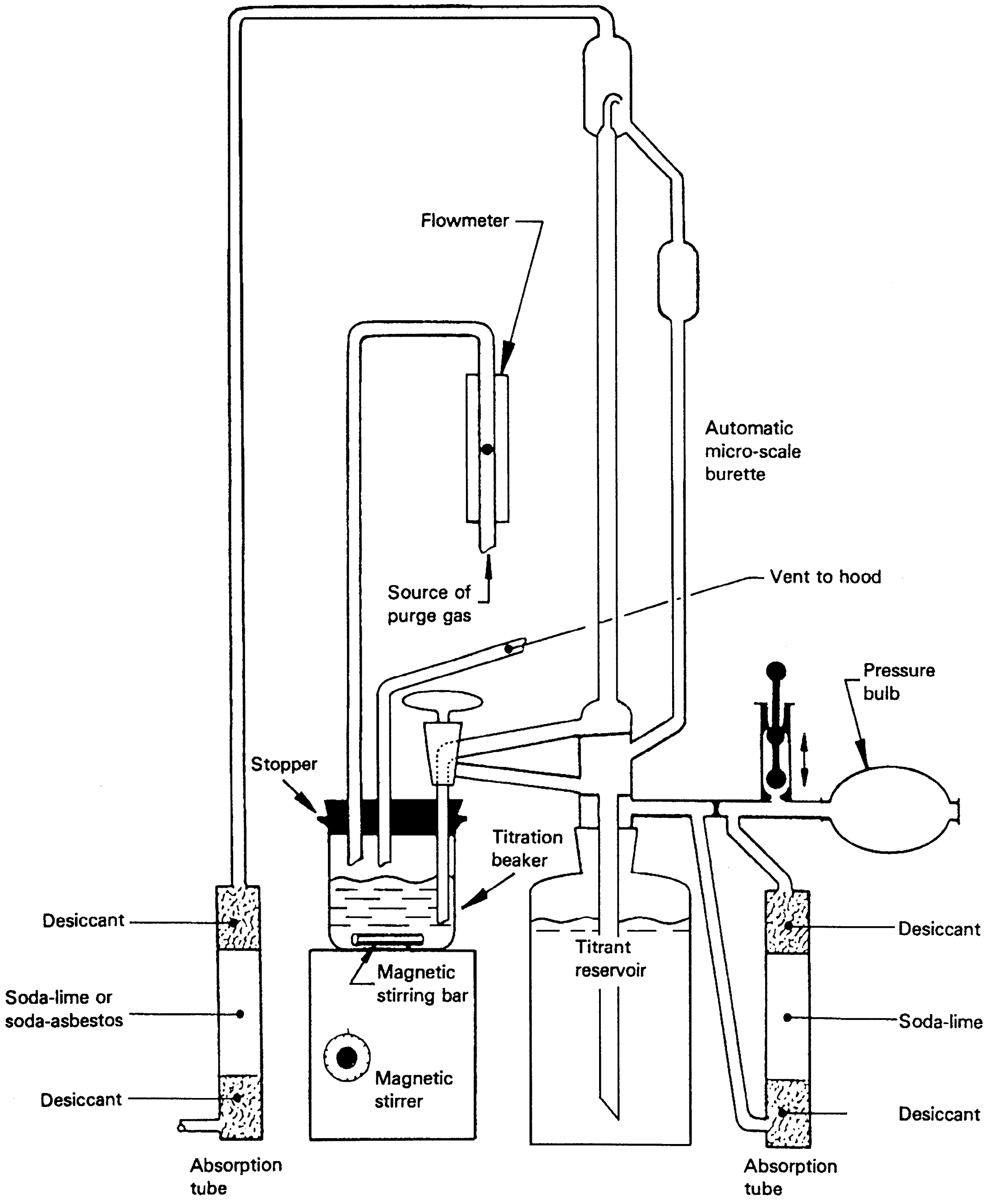

Figure 1 — Schematic drawing of typical apparatus

With either type of reservoir, all entrances and exits to the burette and reservoir shall be connected to absorption tubes to remove atmospheric carbon dioxide and water. These tubes shall contain a desiccant and soda-lime, and precautions shall be taken to prevent introduction of any soda-lime into the reservoir or burette.

NOTE 10 Anhydrous calcium sulfate of particle size 0,71 mm to 1,7 mm is a suitable desiccant.

6.3 Titration beaker, tall-form Berzelius beaker of 100 ml capacity without a spout, of approximate dimensions of 51 mm inside diameter and 71 mm high.

6.4 Titration beaker stopper, composed of elastomeric material (e.g. neoprene) that is essentially unaffected by the titration solvent, and of approximate dimensions of 53 mm top diameter, 45 mm bottom diameter and 25 mm high.

The stopper shall be fitted with a purge gas inlet tube, made of glass and extending 15 mm ± 2 mm beyond the bottom of the stopper, and pierced by a 7 mm ± 1 mm diameter purge gas outlet hole. The inlet tube and outlet hole shall be placed on opposite sides of the stopper with a centre-to-centre separation distance of 30 mm ± 1 mm.

6.5 Purge gas flowmeter, variable area, with a capacity of at least 40 l/h, capable of indicating a flow rate of 10 l/h ± 1 l/h.

6.6 Stirrer motor, variable speed, magnetically linked.

6.7 Stirring bar, cylindrical, polytetrafluorethylene (PTFE) encased, approximately 25 mm long and 8 mm in diameter.

6.8 Pipette, capable of delivering 0,100 ml ± 0,002 ml of titration indicator solution.

6.9 Titration solvent burette, capacity 500 ml or larger, with 5 ml subdivisions. The top of the burette shall be stoppered and connected with an absorption tube, as in 6.2, to remove atmospheric carbon dioxide and water.

NOTE 11 Alternative means of dispensing titration solvent may be used, provided that a dispensing repeatability within ± 1 ml for 40 ml is obtainable and the solvent in the dispenser is isolated from atmospheric carbon dioxide and water.

7 Preparation of used oil samples

7.1 Strictly observe the sample preparation procedure specified in 7.3 to ensure that the sediment, which may be acidic or basic, or have absorbed acidic or basic material from the sample, is evenly dispersed. Failure to obtain a representative sample will lead to erroneous results.

7.2 As used oil may change appreciably in storage, samples shall be tested as soon as possible after removal from the lubricating or test system, and the dates of sampling and testing shall be noted.

7.3 Heat the sample of used oil to 60 °C ± 5 °C in the original container and agitate until all sediment (see note 12) is homogeneously suspended in the oil. If the container is of opaque material, or if it is more than 75 % full, transfer the entire sample to a clear glass bottle having a capacity of at least one-third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by violent agitation of portions of the sample in the original container.

After complete suspension of all sediment, filter the sample, or a convenient aliquot, through a 150 µm wire mesh sieve for the removal of large contaminating particles (see note 10).

NOTE 12 When samples are visibly free of sediment, the heating and filtration procedures may be omitted.

8 Procedure

8.1 Sample titration

8.1.1 Weigh, to the nearest 0,1 mg, the required amount of test portion, as assessed from table 1, into the clean, tared titration beaker (6.3).

Table 1 — Test portion mass[1)]

Acid number mg KOH/g	Sample mass g
less than 0,01	2,0 to 5,0
0,01 to 0,10	1,5 to 2,0
0,10 to 0,5	1,0 to 1,5
0,5 to 3,0	0,2 to 1,0
greater than 3,0	0,1 to 0,2
1) Dark-coloured samples with acid numbers of 0,1 mg KOH/g or less may require use of smaller mass samples to minimize interference of the sample colour with the indicator colours.	

Place the magnetic stirring bar (6.7) in the beaker, taking care not to lose any of the sample by splashing. Pour 40 ml of the titration solvent (5.6) into the titration beaker, using part of this volume to wash down any sample that may have splashed on to the sides of the beaker above the solvent-sample solution level. Add 0,100 ml ± 0,002 ml of the indicator solution (5.1) to the solvent-sample solution. Immediately assemble the titration beaker with the stopper (6.4), previously connected with the flowmeter (6.5) and nitrogen purge gas (5.2).

Insert the burette tip into the beaker through the hole in the stopper. Adjust the position of the burette tip so that the purge gas can exit freely through the hole, and the bottom of the burette tip is approximately 10 mm above the surface of the solution. Immediately start the purge gas flow through the beaker at a relatively fast rate (30 l/h to 40 l/h), to purge the atmosphere in the beaker rapidly, and then start mixing the solution using the magnetic stirrer. Adjust the purge gas flow rate to 10 l/h ± 1 l/h after purging at the faster flow rate for 15 s to 30 s. Adjust the stirring rate to mix the solution efficiently but without splashing the solution or mixing purge gas into the solution.

CAUTION — The purge gas shall be able to exit freely, or dangerous pressures could develop. In addition, this vapour contains toluene which requires removal with adequate ventilation.

8.1.2 Titrate the sample at a temperature below 30 °C with the potassium hydroxide solution (5.7). During the titration, the indicator colour changes from the initial orange to a bright yellow and then to green. The end-point is the first appearance of the stable green colour that does not revert to a yellow or yellow-green within 15 s to 20 s. Record the volume of titrant required to obtain the stable end-point.

NOTE 13 The end-point can be anticipated by the initial change to yellow, which occurs very close to the end-point.

NOTE 14 Several drops of titrant may be required to obtain the stable end-point colour after reaching a yellow-green colour with used oil samples having relatively high acid numbers, for example approximately 3 mg KOH/g or greater.

8.2 Blank titration

Carry out a blank titration each day that samples are analysed. Conduct this titration using the procedure specified in 8.1, but omitting the sample. Record the volume of titrant required to obtain the stable end-point.

9 Calculation

Calculate the acid number of the sample, AN, in milligrams of potassium hydroxide per gram of sample (mg KOH/g), using the equation:

$$\text{AN} = 56{,}1 \times c \times \frac{(V_3 - V_0)}{m}$$

where

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

V_0 is the volume, in millilitres, of titrant required for the blank;

V_3 is the volume, in millilitres, of titrant required for the determination;

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

10 Expression of results

Report the result to the nearest 0,01 mg KOH/g for acid numbers of 0,10 mg KOH/g and below, and to the nearest 0,1 mg KOH/g for acid numbers above 0,10 mg KOH/g.

11 Precision

The precision, as determined by statistical examination of inter-laboratory test results, is given in 11.1 and 11.2 below, and is illustrated in figure 2.

The precision was determined on turbine oils with acid numbers between 0,05 mg KOH/g and 20,0 mg KOH/g only. Insufficient data are available on other oil types or higher acid numbers within the scope of this method to assess the validity of these values for such products.

11.1 Repeatability

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

$r = 0{,}08\ (X)^{0{,}5}$

where X is the mean of the values being compared.

11.2 Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the normal and correct operation of the test method, exceed the value below in only one case in twenty.

$R = 0{,}27\ (X)^{0{,}5}$

where X is the mean of the values being compared.

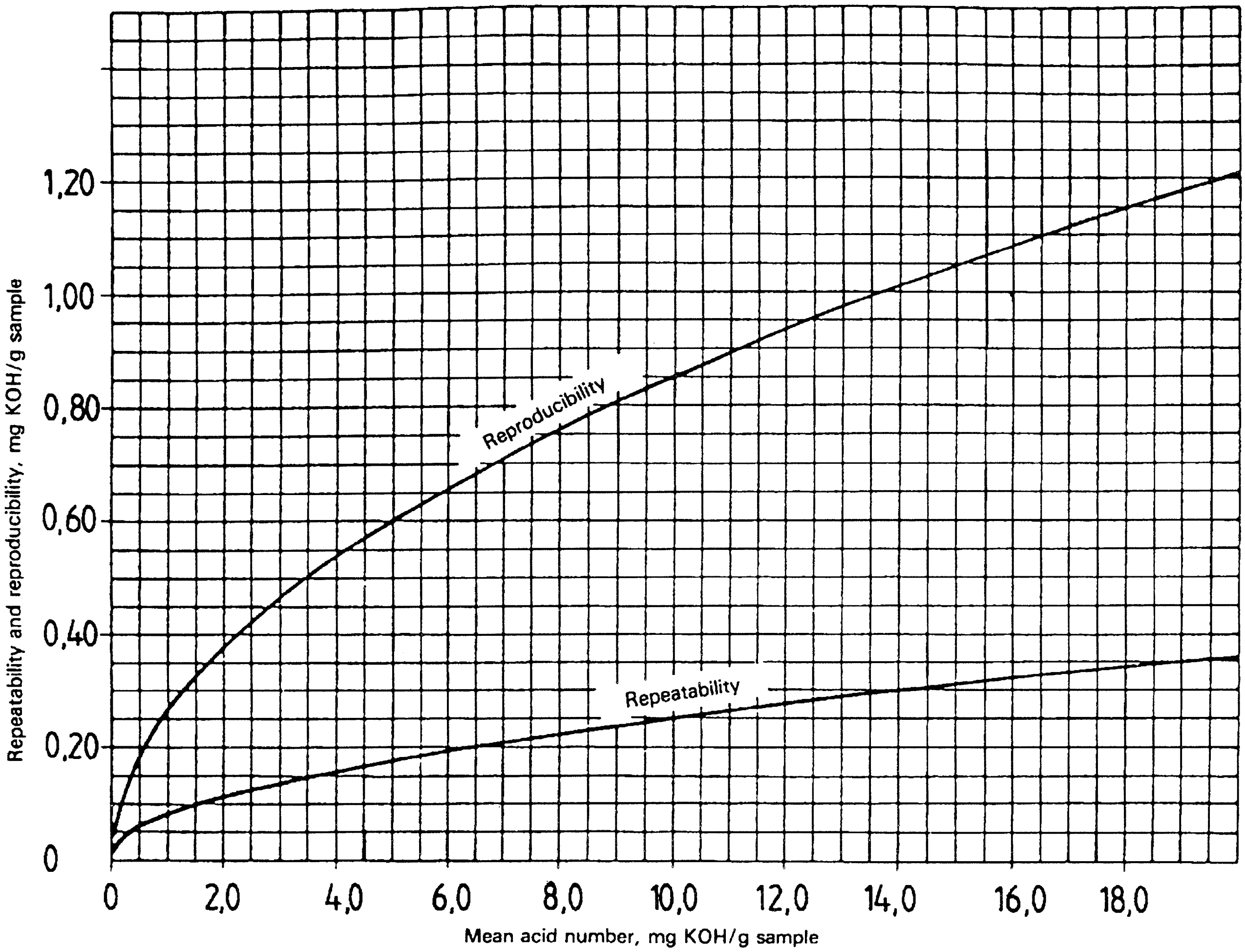

Figure 2 — Precision curves

12 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

b) the type and complete identification of the product tested;

c) the result of the test (see clause 10);

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

e) the date of the test.

Annex A
(informative)

Bibliography

[1] ISO 4263:1986, *Petroleum products — Inhibited mineral oils — Determination of oxidation characteristics.*

[2] ISO 6619:1988, *Petroleum products and lubricants — Neutralization number — Potentiometric titration method.*

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