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INTERNATIONAL STANDARD

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

Produits pétroliers — Détermination de l'indice d'acide total — Semi-microméthode de titrage par indicateur coloré

Reference number
ISO 7537 : 1989 (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 approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 7537 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants.*

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

1 Scope

1.1 This International Standard specifies a semi-micro colour indicator titration method for the determination of acidic constituents in new or used petroleum products and lubricants soluble in mixtures of toluene and isopropyl alcohol, or capable of existing as suspensions in such mixtures.

The method is especially intended for applications in which the amount of sample available to be analyzed 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}.

1.2 This method may be used to indicate relative changes in total 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.

1.3 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 total acid number by

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

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

NOTES

1 Some oils, such as many cutting oils, rustproofing oils, and similar compounded oils, or excessively dark-coloured oils, may be more difficult to analyze 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, due to the use of a more highly dilute sample during the titration and due to the greater stability of the end-point colour change. 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.

2 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 total acid numbers obtained using both titration methods for the samples used for the precision statement (see 9.2).

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

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

ISO 6618 : 1987, *Petroleum products and lubricants — Neutralization number — Colour-indicator titration method.*

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

3 Principle

Determination of the total acid number by dissolving a sample of the oil in a solvent consisting of toluene, isopropyl alcohol, and a small amount of water. The resulting single-phase solution is titrated at room temperature under a nitrogen atmosphere with a standard potassium hydroxide (KOH) solution in isopropyl alcohol, $c(\text{KOH}) = 0{,}01$ mol/l, to the stable green colour of the added *p*-naphtholbenzein indicator.

4 Definition

total acid number: The quantity of KOH, expressed in milligrams, required to titrate all acids or salts present in one gram of the sample having dissociation or hydrolysis constants larger than 10^{-9}.

5 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade. All reference to water shall be understood to mean freshly distilled (carbon dioxide free) water.

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

5.2 Nitrogen, dry and carbon dioxide free.

NOTE — 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

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

5.4 Titration solvent

Add 500 ml of toluene and 5 ml of water to 495 ml of anhydrous isopropyl alcohol.

5.5 Potassium hydroxide, alcoholic solution, standard volumetric, $c(\text{KOH}) = 0{,}01$ mol/l.

5.5.1 Preparation

Add 3 g of solid KOH to approximately 1 litre of anhydrous isopropyl alcohol (containing less than 0,9 % water) in a 2 litre 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 about 1 g of barium hydroxide and again boil gently for about 10 min.

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

Filter the supernatant liquid through a 10 µm polytetrafluoroethylene (PTFE) membrane filter while avoiding unnecessary exposure to the atmosphere and then dilute the solution (approximately 0,05 mol/l) with the anhydrous isopropyl alcohol to a total volume of about 5 litres to obtain a final concentration of 0,010 mol/l ± 0,002 mol/l.

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 — Because of the relatively large coefficient of cubic expansion of organic liquids such as isopropyl alcohol, the standard alcoholic solutions should be standardized at temperatures close to those employed in the titrations of samples.

5.5.2 Standardization

Standardize the titrant against dried (at least 1 h at 110 °C), pure potassium hydrogen phthalate using the method specified in 8.1 for the total acid number analysis, but using water (40 ml ± 1 ml) as the solvent and 6 drops of phenolphthalein solution as the indicator.

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

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

5.6 Toluene, complying with the requirements of ISO 6353-2.

6 Apparatus

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

6.2 Titrant reservoir, preferably one which is integral with the automatic burette, such as that shown in figure 1.

If a titrant reservoir separate from the automatic burette is used, the line connecting the reservoir with the burette shall be all glass.

Exposure of the titrant to light shall be minimized by the use of amber glass for the reservoir, by wrapping the reservoir with foil such as aluminium foil, or by other suitable means.

The tube in the reservoir for titrant withdrawal shall be adjusted so that the end of the tube is about 20 mm from the bottom of the reservoir so that any precipitate that may collect on the bottom of the reservoir will not be disturbed. To further avoid disturbing any precipitate in the reservoir, movement of the reservoir shall be minimized.

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 may contain, for example, 0,71 to 1,7 mm anhydrous calcium sulfate as desiccant and soda-lime to absorb carbon dioxide. Precautions shall be taken to prevent introduction of any soda-lime into the titrant reservoir or burette.

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

6.4 Titration beaker stopper, to seal the titration beaker.

The stopper shall be composed of an elastomeric material, such as neoprene, that is essentially unaffected by the titration solvent.

Approximate stopper dimensions are 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, capable of indicating a flow rate of 10 litres/h.

6.6 Stirrer motor, variable speed, magnetically linked.

6.7 Stirring bar, cylindrical, 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.

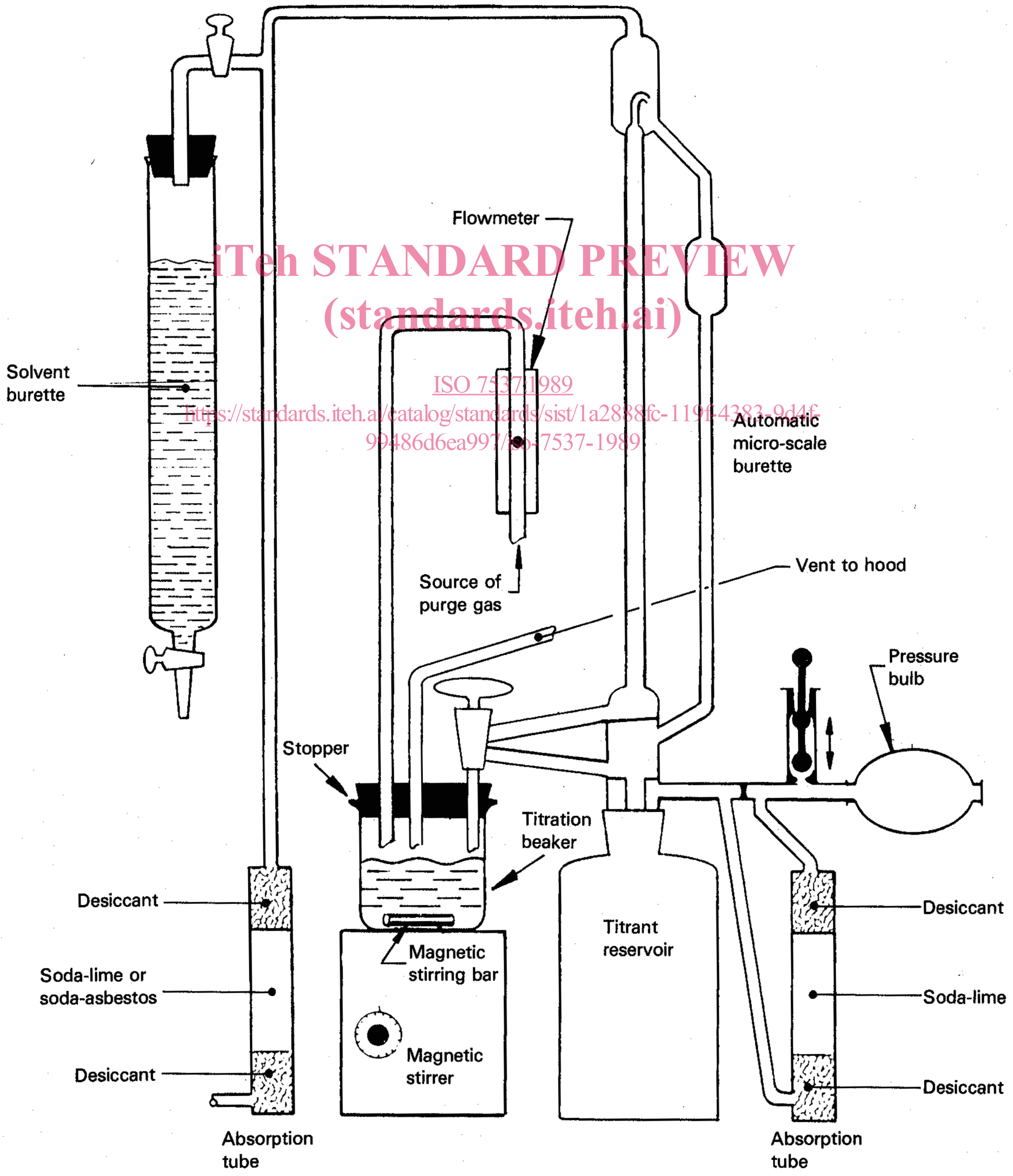

Figure 1 — Schematic drawing of typical apparatus

6.9 Titration solvent burette, capacity 500 ml or larger, with 5 ml subdivisions.

The top of the titration solvent burette shall be stoppered and connected with an absorption tube, as in 6.2, to remove atmospheric carbon dioxide and water. An alternative means of dispensing the 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 Strict observance of the sample preparation procedure specified in 7.2 is necessary, since the sediment itself may be acidic or basic or may have absorbed acidic or basic material from the sample. Failure to obtain a representative sample may lead to erroneous results.

7.2 Heat the sample (see note 1) of used oil to 60 °C ± 5 °C in the original container and agitate until all sediment is homogeneously suspended in the oil (see also note 2).

If the original container is of opaque material, or if it is more than three-quarters full, transfer the entire sample to a clear glass bottle having a capacity 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, strain the sample or a convenient aliquot of the sample through a 150 µm screen for the removal of large contaminating particles (see note 3).

NOTES

1 When samples are visibly free of sediment, the heating procedure may be omitted.

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

3 When samples are visibly free of sediment, the straining procedure 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 into the clean, tared titration beaker (6.3). Guidelines for determining the amount of test portion required are given in table 1.

Table 1 — Size of sample[1]

Total acid number range mg KOH/g sample	**Sample weight range** g
less than 0,01	5,0 to 2,0
0,01 to 0,1	2,0 to 1,5
0,1 to 0,5	1,5 to 1,0
0,5 to 3,0	1,0 to 0,2
greater than 3,0	0,2 to 0,1

[1] Dark-coloured samples with total acid numbers of 0,1 or less may require use of smaller size samples to minimize interference of the sample colour with the indicator colours.

Place the magnetic stirring bar (6.7) into the beaker, taking care not to lose any of the sample by splashing. Pour 40 ml of the titration solvent (5.4) into the titration beaker, using part of this volume of solvent 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 *p*-naphtholbenzein 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 (see CAUTION), 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, for example about 30 to 40 litres/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 litres/h ± 1 litre/h after purging at the faster flow rate for 15 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 must be able to exit freely, otherwise dangerous pressures could develop. Also, the vapour from this treatment contains toluene and should be removed with adequate ventilation.

8.1.2 Titrate the sample at a temperature below 30 °C with the standard volumetric potassium hydroxide solution (5.5).

The indicator colour changes are from the initial orange to a bright yellow and then to green. Take the point at which a stable green colour is first obtained as the end-point. Consider the colour stable if it does not change back to a yellow or yellow-green colour within 15 to 20 s (see the note). This end-point can be anticipated by the initial change to yellow, which occurs very close to the end-point. Record the quantity of titrant required to obtain the stable end-point.

NOTE — 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 total acid numbers, for example a total acid number of about 3 or greater.

8.2 Blank titration

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

9 Expression of results

9.1 Method of calculation

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

$$\mathrm{TAN} = 56{,}1 \times c \times \frac{(V_1 - V_0)}{m}$$

where

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

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

V_1 is the volume, in millilitres, of titrant required for the determination;

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

Report the result as the total acid number. In general, the TAN is reported to one decimal place, but may be reported to two decimal places if it is a very low acid number (e.g. 0,05).

9.2 Precision

9.2.1 This precision section applies to turbine oils. Insufficient data are available on other oils coming within the scope of this method to permit the precision to be given for such oils.

9.2.2 The precision of the method, as obtained by statistical examination of inter-laboratory test results, is as follows:

9.2.2.1 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 long run, in the normal and correct operation of the test method, exceed the value shown below (and those in figure 2) in only one case in 20.

Total acid number	**Repeatability**
0,05 to 20,0	$0{,}08\ (X)^{1/2}$

where X is the mean total acid number of the sample.

9.2.2.2 Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the value shown below (and those in figure 2) only in one case in 20.

Total acid number	**Reproducibility**
0,05 to 20,0	$0{,}27\ (X)^{1/2}$

where X is the mean total acid number of the sample.

10 Test report

The test report shall contain at least the following information:

a) the type and identification of the product tested;

b) a reference to this International Standard;

c) the result of the test (see 9.1);

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

e) the date of the test.

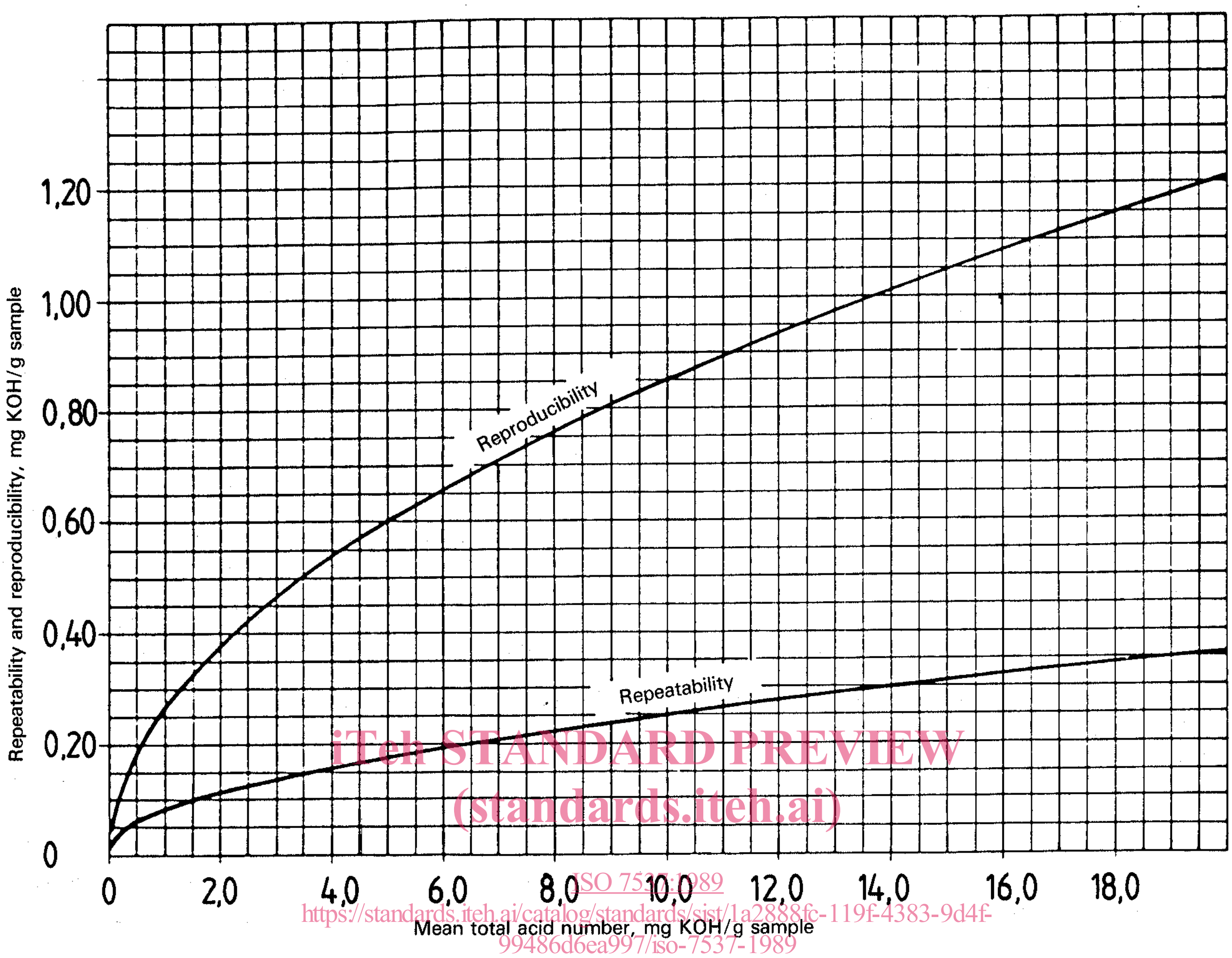

Figure 2 — Precision curves

UDC 665.7 : 543.852.1

Descriptors : petroleum products, chemical analysis, determination of content, acid number, apparatus, acidimetry, volumetric analysis.

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