INTERNATIONAL
STANDARD

ISO
6293-1

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Petroleum products — Determination of saponification number —

Part 1:
Colour-indicator titration method

Produits pétroliers — Détermination de l'indice de saponification —

Partie 1: Méthode par titrage avec indicateur coloré

Reference number
ISO 6293-1:1996(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 6293-1 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This first edition cancels and partially replaces the first edition of ISO 6293:1983, which has been technically revised.

ISO 6293 consists of the following parts, under the general title *Petroleum products — Determination of saponification number*:

— *Part 1: Colour-indicator titration method*

— *Part 2: Potentiometric titration method*

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Petroleum products — Determination of saponification number —

Part 1:
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 part of ISO 6293 specifies a method for the determination, by colour-indicator titration, of the amount of constituents in petroleum products that will saponify under the conditions of the test.

The method is applicable to materials having saponification numbers in the range 2 mg/g KOH to 200 mg/g KOH.

Compounds of sulfur, phosphorus, halogens and some other compounds interfere by reacting with the alkali and acids under the test conditions.

NOTES

1 The results on used crankcase and turbine oils, and on oils containing the interfering compounds above as additive constituents, should be interpreted with care, bearing in mind the possible higher values obtainable due to these additional reactants.

2 The interfering compounds above are contained in extraneous materials including certain organic acids and most nonalkali soaps. The odour of hydrogen sulfide near the end of the back-titration step is an indication of the presence of certain reactive sulfur compounds, but other reactive sulfur compounds, as well as those of chlorine, phosphorus and other interfering materials, give no simple indication during the test. A gravimetric determination of fatty acid content is an alternative procedure for the estimation of such compounds.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 6293. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 6293 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 6353-2:1983, *Reagents for chemical analysis — Part 2: Specifications — First series.*

ISO 6353-3:1987, *Reagents for chemical analysis — Part 3: Specifications — Second series.*

3 Definitions

For the purposes of this part of ISO 6293, the following definitions apply.

3.1 saponify: To hydrolyze a fat with alkali to form an alcohol and the salt of a fatty acid.

3.2 saponification number: The number of milligrams of potassium hydroxide consumed by 1 g of a sample under the specified conditions of this test.

4 Principle

A test portion of petroleum product of known mass, dissolved in butan-2-one, is reacted by heating with a known amount of alcoholic potassium hydroxide solution. The excess alkali is titrated with standard volumetric hydrochloric acid solution, using phenolphthalein as indicator, and the saponification number calculated.

5 Reagents and materials

During the analysis, use only reagents specified in ISO 6353-2 and ISO 6353-3, if listed there, or if not, of recognized analytical grade. Use only distilled water or water to grade 3 of ISO 3696.

5.1 Ethanol, 95 % (V/V) ethanol, or a solution comprising 90 % (V/V) of 95 % (V/V) ethanol and 10 % (V/V) of methanol, or absolute ethanol.

NOTE — Studies have shown that 99 % (V/V) propan-2-ol can be substituted for the ethanol in routine analysis with equivalent sensitivity and precision, but should not be used in referee tests.

5.2 Potassium hydroxide, c(KOH) = 0,5 mol/l, standard volumetric alcoholic solution, prepared in accordance with 5.2.1 or obtained commercially, and standardized in accordance with 5.2.2.

5.2.1 Preparation

Add approximately 29 g of solid KOH to 1 l of ethanol (5.1) in a 2-litre conical flask. Boil gently with stirring for 10 min to 15 min. Add at least 2 g of barium hydroxide [$Ba(OH)_2$] and boil gently for a further 5 min to 10 min.

Allow to cool and stand at room temperature for at least 24 h in the dark. Transfer to the storage container by filtration or pressure displacement under inert gas conditions (carbon dioxide-free).

Store the solution 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 or nonfibrous soda silicate absorbent (Ascarite, Carbosarb or Indecarb)[1]. Glass bottles are not recommended for storage.

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[1] Ascarite, Carbosarb and Indecarb are examples of suitable products available commercially. This information is given for the convenience of users of this part of ISO 6293 and does not constitute an endorsement by ISO of these products.

5.2.2 Standardization

Standardize frequently enough to detect changes of 0,000 5 mol/l, preferably against 2,0 g to 2,1 g of pure potassium acid phthalate (5.7), which has been dried for 1 h at 100 °C, weighed with an accuracy of ± 0,000 2 g and dissolved in 100 ml ± 0,01 ml of carbon dioxide-free water, using phenolphthalein (5.6) to detect the end-point.

5.3 Hydrochloric acid, c(HCl) = 0,5 mol/l, standard volumetric alcoholic solution, prepared in accordance with 5.3.1 or obtained commercially, and standardized in accordance with 5.3.2.

5.3.1 Preparation

Mix 45 ml of concentrated hydrochloric acid [35,4 % (m/m)] with 1 l of ethanol (5.1).

5.3.2 Standardization

Standardize frequently enough to detect changes of c(HCl) = 0,000 5 mol/l, preferably by electrometric titration of approximately 8 ml (accurately measured) of the 0,5 mol/l alcoholic potassium hydroxide solution (5.2) diluted with 125 ml of carbon dioxide-free water.

NOTES

1 Because of the relatively large coefficient of cubic expansion of organic liquids such as ethanol or propan-2-ol, the standard alcoholic solutions should be standardized at temperatures close to those employed in the titrations of sample, and close to 20 °C.

2 Where saponification numbers below 2 are expected, better precision may be obtained by substituting potassium hydroxide and hydrochloric acid solutions of concentration 0,1 mol/l for the reagents of concentration 0,5 mol/l in 5.2 and 5.3, and those in clauses 7 and 8. No exact precision values are yet available for this technique.

5.4 Butan-2-one (methyl ethyl ketone), technical grade.

Store the butan-2-one in a dark or brown glass bottle.

5.5 Petroleum spirit, 60 °C to 80 °C boiling range.

5.6 Phenolphthalein, neutralized indicator solution.

Dissolve 1,0 g of phenolphthalein in 100 ml ethanol (5.1) and neutralize to a faint pink colour with ethanolic potassium hydroxide solution, c(KOH) = 0,1 mol/l.

5.7 Potassium acid phthalate.

6 Apparatus

Ordinary laboratory apparatus and glassware, including:

6.1 Conical flask and condenser. A conical flask, 250 ml or 300 ml capacity, alkali-resistant, to which is attached a straight or mushroom-type reflux condenser. The straight condenser shall be fitted to the flask by means of a ground-glass joint; the mushroom-type condenser shall fit loosely to permit venting of the flask.

All glassware shall be chemically clean. The flasks should be cleaned by nonalkaline cleaning agents to match the cleanliness obtained by the use of chromosulfuric acid (see warning). For comparison of cleaning efficiency, the visual appearance and loss in mass on heating may be used. Detergent cleaning, or the use of other strong oxidizing agents, avoids the specific hazards related to chromosulfuric acid, and is preferred for routine analysis. Flasks of borosilicate glass are preferred. New flasks may give high values, and old flasks that have become etched by long use should not be used. Blank tests should be run concurrently on both used and new flasks.

WARNING — Chromosulfuric acid is a health hazard. It is toxic, a recognized carcinogen as it contains Cr(VI) compounds, highly corrosive and potentially hazardous in contact with organic materials. When using chromosulfuric acid cleaning solution, eye protection and protective clothing are essential. Never pipette the cleaning solution by mouth. After use, do not pour cleaning solution down the drain, but neutralize it with great care owing to the concentrated sulfuric acid present, and dispose of it in accordance with standard procedures for toxic laboratory waste (chromium is highly dangerous to the environment).

Non-chromium-containing, strongly oxidizing acid cleaning solutions are also highly corrosive and potentially hazardous in contact with organic materials, but do not contain chromium which has special disposal problems.

6.2 Hotplate, heated by either electricity or steam.

6.3 Titration burette, of capacity 50 ml, graduated in 0,1 ml subdivisions, or of capacity 10 ml, graduated in 0,05 ml subdivisions.

6.4 Balance, capable of weighing to the nearest 0,2 mg.

7 Blank run

7.1 Carry out one or more blank determinations concurrently with each set of samples in the manner described in 7.2 and 7.3.

Blank determinations should be run in duplicate on samples requiring the highest accuracy. The precision data are based on duplicate blank determinations. A single blank is sufficient for routine work.

7.2 Measure from a burette or pipette into the conical flask (6.1) 25 ml ± 0,03 ml of the alcoholic potassium hydroxide solution (5.2) and 25 ml ± 1 ml of the butan-2-one (5.4). If a volumetric pipette is used, wait 30 s after delivery for complete drainage.

Connect the condenser to the flask, and heat for 30 min after refluxing begins.

NOTE 1 It is known that some fats are readily saponified and complete saponification takes place within 10 min after refluxing begins. On the other hand, some materials are saponifiable only with difficulty, and are known to require more than 2 h in some cases. Neither the shortened period nor the longer period should be used except by mutual consent of the interested parties. The reflux time of the blank should be the same as that of the sample in all cases.

Turn off the heat source and immediately add 50 ml of the petroleum spirit (5.5) by cautiously pouring it down the condenser (disconnect the condenser if a mushroom-type is used).

NOTE 2 Pouring 50 ml of petroleum spirit down the condenser at the end of the saponification not only rinses the condenser but also cools the reaction mixture. However, in the case of insulating oils, the addition of petroleum spirit is not necessary.

7.3 Titrate the blank while hot, without reheating, with the hydrochloric acid solution (5.3), using three drops of the phenolphthalein indicator solution (5.6).

When the indicator colour has disappeared, add, drop by drop, more indicator solution. If this addition of indicator restores the colour, continue the titration, making further drop-by-drop additions of indicator, if necessary, until the end-point is reached. The end-point is reached when the indicator colour has completely disappeared and does not immediately reappear upon further drop-by-drop addition of the indicator solution.

To avoid emulsification of the titration mixture, but assure phase contact, swirl the flask vigorously as the end-point is approached.

8 Test procedure

8.1 Test portion

Estimate the saponification number and select a test portion mass from table 1.

NOTE — The mass is based on an anticipated back-titration of between 40 % and 80 % of the blank, with a maximum test portion of 20 g.

Table 1 — Mass of test portion

Estimated saponification number mg/g KOH	**Mass of test portion** g
181 to 400	1
111 to 180	2
71 to 110	3
31 to 70	5
16 to 30	10
0 to 15	20

8.2 Determination

8.2.1 Weigh the test portion, to the nearest 0,01 g, into the conical flask (6.1). Add 25 ml ± 1 ml of the butan-2-one (5.4) followed by 25 ml ± 0,03 ml of the alcoholic potassium hydroxide solution (5.2), measured from a burette or pipette (see 7.2). Connect the condenser to the flask and heat for 30 min after refluxing begins (see 7.2). Turn off the heat source and immediately add 50 ml of the petroleum spirit (5.5) by cautiously pouring it down the condenser (disconnect the condenser if a mushroom-type is used).

8.2.2 Titrate while hot with the hydrochloric acid solution (5.3) as specified in 7.3.

NOTE — When testing waxes, it may be necessary to reheat the solution during titration to prevent solidification of the sample.

9 Calculation

Calculate the saponification number, SN, in milligrams of KOH per gram of sample, from equation (1).

$$\mathrm{SN} = \frac{(V_0 - V_1)\, c_{\mathrm{HCl}} \times 56{,}1}{m} \qquad \ldots (1)$$

where

V_1 is the volume, in millilitres, of hydrochloric acid solution required for titration of the test portion;

V_0 is the volume, in millilitres, of hydrochloric acid solution required for titration of the blank solution;

c_{HCl} is the concentration, in moles per litre, of the standard volumetric hydrochloric acid solution;

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

10 Expression of results

Report the results, calculated in clause 9, as saponification number (milligrams KOH per gram sample), as follows.

For electrical insulating oils:	to the nearest 0,1;
for saponification numbers below 50:	to the nearest 0,5;
for saponification numbers of 50 and above:	to the nearest 1.

11 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is given in 11.1 and 11.2, and is illustrated in figure 1.

NOTE — No precision can be given for highly-coloured new or used oils, or for oils which produce dark-coloured solutions upon saponification, as colour may interfere with the detection of the end-point of the titration.

11.1 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 in only one case in 20.

$$r = 0{,}26\sqrt{x}$$

where x is the average of the two results being compared.

11.2 Reproducibility, R

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 20.

$$R = 0{,}74\sqrt{x}$$

where x is the average of the two results being compared.

12 Test report

The test report shall contain at least the following information:

a) a reference to this part of ISO 6293;

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

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

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

e) the date of the test.

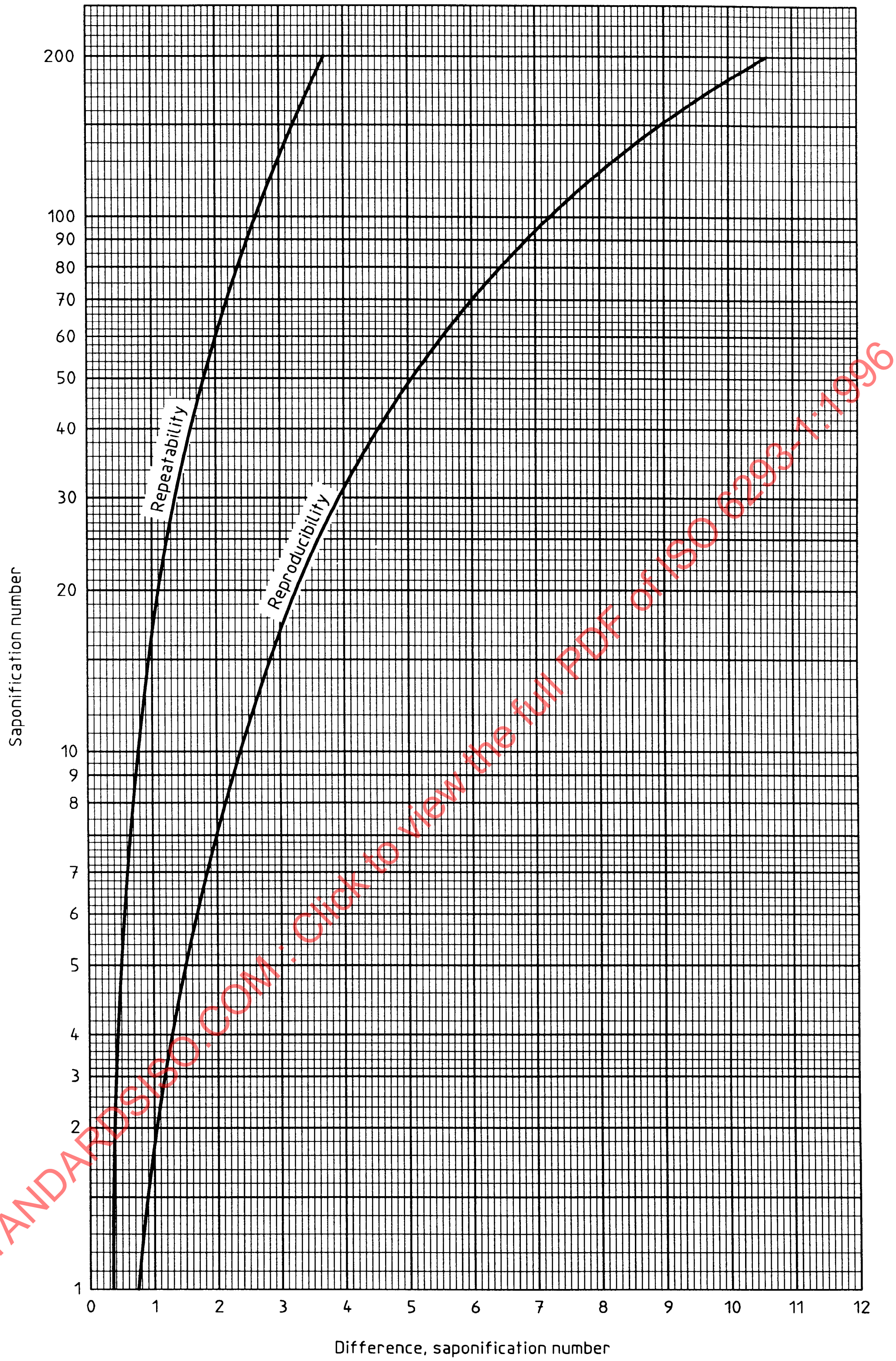

Figure 1 — Precision data