INTERNATIONAL STANDARD

ISO 6293-2

First edition
1998-05-01

Petroleum products — Determination of saponification number —

Part 2:
Potentiometric titration method

Produits pétroliers — Détermination de l'indice de saponification —

Partie 2: Méthode par titrage potentiométrique

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Reference number
ISO 6293-2:1998(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 6293-2 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants.*

This first edition, together with ISO 6293-1, cancels and replaces 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*

Annex A forms an integral part of this part of ISO 6293.

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Petroleum products — Determination of saponification number —

Part 2:
Potentiometric titration method

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WARNING — The use of this part of ISO 6293 may involve hazardous materials, operations and equipment. This part of ISO 6293 does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this part of ISO 6293 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 potentiometric titration, of the amount of constituents in petroleum products that will saponify under the conditions of the test. ISO 6293-1 specifies a determination by colour indicator titration.

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

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

NOTES

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

2 These extraneous materials include certain organic acids and most non-alkali 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 6293-1:1996, *Petroleum products — Determination of saponification number — Part 1: Colour-indicator titration method.*

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 that is consumed by 1 g of a sample under the specified conditions of this test

4 Principle

A test portion of known mass, dissolved in butan-2-one, is heated with a known amount of alcoholic potassium hydroxide solution. The excess alkali is potentiometrically titrated with standard volumetric hydrochloric acid solution and the saponification number is 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 according to grade 3 of ISO 3696.

5.1 Ethanol, 95 % (*V/V*) ethanol, or 9 parts of 95 % (*V/V*) ethanol to which has been added 1 part of methanol or absolute alcohol.

NOTES

1 For the purposes of this part of ISO 6293, the expressions "% (*m/m*)" and "% (*V/V*)" are used to represent the mass and volume fractions of a material respectively.

2 For routine analysis, 99 % (*V/V*) propan-2-ol can be substituted for ethanol without compromising the sensitivity or precision of the method. Ethanol should always be used for referee tests.

5.2 Potassium hydroxide, c(KOH) = 0,5 mol/l, standard volumetric alcoholic solution.

Prepare in accordance with 5.2.1 or use a commercially available solution. Standardize in accordance with 5.2.2.

5.2.1 Preparation

Add approximately 29 g of solid KOH to 1 litre of ethanol (5.1) in a 2 litre conical flask. Boil gently while 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.

CAUTION — Barium hydroxide is strongly alkaline and toxic if ingested. Use protective clothing to avoid severe irritation caused by contact with the skin.

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 non-fibrous soda silicate absorbent. Glass bottles are not recommended for storage.

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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 110 °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 aqueous solution.

Prepare in accordance with 5.3.1 or use a commercially available solution. Standardize in accordance with 5.3.2.

5.3.1 Preparation

Mix 45 ml of concentrated hydrochloric acid [35,4 % (*m/m*)] with 1 litre of water.

5.3.2 Standardization

Standardize frequently enough to detect changes of 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 0,1 mol/l potassium hydroxide and hydrochloric acid solutions for the 0,5 mol/l reagents 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 (methylethylketone),** reagent grade.

NOTE — 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 of ethanol (5.1) and neutralize to a faint pink colour with 0,1 mol/l ethanolic potassium hydroxide solution.

5.7 **Potassium acid phthalate.**

5.8 **Potassium chloride,** 3,0 mol/l aqueous solution.

Dissolve 225 g of solid potassium chloride (KCl) in 1,0 litre of water.

5.9 **Xylene.**

5.10 **Chlorobenzene.**

CAUTION — Chlorobenzene is harmful to the environment. Alternative solvents are under investigation.

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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 (see the following note), to which is attached a straight or mushroom-type reflux condenser. The straight-type 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.

NOTE — The flasks should be cleaned by non-alkaline cleaning agents to match the cleanliness obtained by the use of chromosulfuric acid (see warning). For the 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 Potentiometric titrator, of high precision, capable of distinguishing the carbonate ion from the hydroxide ion in the titration of reagent grade potassium hydroxide (KOH) by hydrochloric acid. Automatic, recording or manual apparatus are suitable.

6.4 Electrodes, of high quality. The cleaning and maintenance of the electrodes are described in annex A.

6.4.1 Combination glass electrode, or a suitable glass electrode and a suitable reference electrode.

NOTE — Either silver chloride (AgCl), saturated lithium chloride (LiCl) or saturated potassium chloride (KCl)/calomel electrodes are suitable reference electrodes.

6.5 Stirrer, either magnetic stirring bars or a propeller stirrer, capable of providing very vigorous agitation.

NOTE — The optimum magnetic stirring bar has been found to be a 25 mm × 5 mm plain polytetrafluoroethylene (PTFE) coated cylinder.

6.6 Beakers, of capacity 250 ml or 300 ml, tall form, with or without spout.

6.7 Titration assembly, typically as illustrated in figure 1.

6.7.1 Stirrer, of variable speed, either mechanical or electrical, with propeller or paddle of inert material, or a magnetic stirrer with stirring bars (6.5). All electrical devices shall be grounded (earthed) so that no permanent change to the meter reading occurs during the course of the titration.

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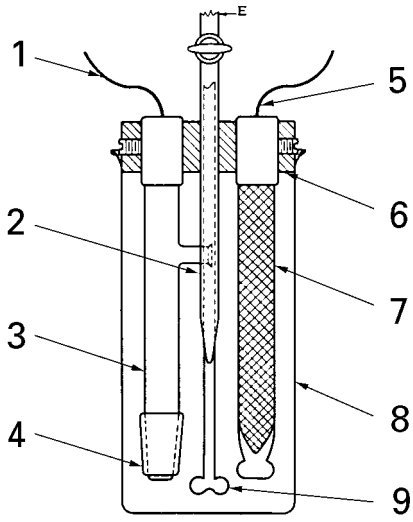

Key

1 Lead for reference electrode
2 Elongated burette tip (in front of stirrer)
3 Reference electrode, B
4 Sleeve with ground-glass contact joint
5 Shielded lead for glass electrode
6 Bakelite support
7 Glass electrode, C (internally shielded)
8 Beaker, A
9 Propeller stirrer, D (behind burette tip)

Figure 1 — Typical titration cell assembly

6.7.2 Burette, manual or automatic, of capacity 10 ml or 25 ml, graduated in 0,05 ml divisions, and calibrated with an accuracy of ± 0,02 ml.

6.7.3 Titration stand, capable of supporting the beaker, electrodes, stirrer and burette.

NOTES

1 An arrangement that allows for the removal of the beaker without disturbing the electrodes, burette and stirrer is desirable.

2 Some apparatus is sensitive to interference by static electricity, shown by erratic movements of the recorder pen or meter indicator, when the titration assembly is approached by the operator. If this occurs, surround the beaker closely with a cylinder of copper gauze that is electrically grounded (earthed).

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

7 Blank test

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.

NOTE — 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. Duplicate blank determinations should agree within 0,5 ml. Take the average for calculations (see clause 9).

7.2 Measure, from a burette or pipette (see note 1 in this subclause) 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). Connect the condenser to the flask and heat for 30 min after refluxing begins (see note 2 in this subclause). Turn off the heat source and immediately add 50 ml of the petroleum spirit (5.5) (see notes 3 and 4 in this subclause) by cautiously pouring it down the condenser (disconnect the condenser if a mushroom-type is used).

NOTES

1 If a volumetric pipette is used, wait 30 s after delivery for complete drainage.

2 Standard procedure requires that the mixture is refluxed for 10 min. However, it is known that some fats are readily saponified and complete saponification takes place within 10 min. On the other hand, some materials are saponifiable only with

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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.

3 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.

4 In the case of insulating oils, the addition of petroleum spirit is not necessary.

7.3 Titrate the blank potentiometrically while hot, without reheating, with the hydrochloric acid solution (5.3).

7.4 Transfer the solution to a beaker (6.6). Wash the flask with two 10 ml portions of petroleum spirit, and add these washings to the beaker.

7.5 Place the beaker, with a magnetic stirring bar if used, on the titration stand (fitted with a magnetic stirplate if stirring bars are included). Immerse the electrodes as far as possible, without interfering with the stirrer or stirring bars. Stir to the maximum agitation without causing excessive aeration or splattering of the solution.

7.6 Titrate the blank solution with aqueous hydrochloric acid (5.3), added at the rate of 2 ml/min, using the potentiometric titrator.

NOTE — Two inflections with corresponding equivalence points are expected. The first one corresponds to the free potassium hydroxide (KOH), and the second to the small amount of potassium carbonate (K_2CO_3) generally present in commercial KOH.

7.7 Record the first inflection point.

NOTE — A pre-addition of hydrochloric acid titrant can be used in the blank to expedite the titration.

8 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 KOH/g	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

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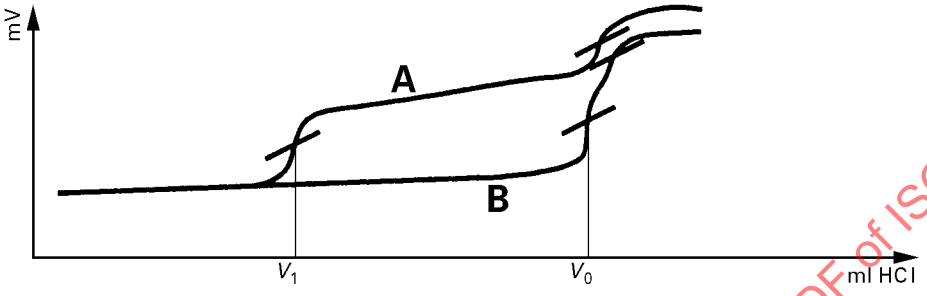
pipette (see note 1 in 7.2). Dissolve the difficult to dissolve samples first in 15 ml to 25 ml of xylene (5.9), before adding the butan-2-one.

8.2.2 Connect the condenser to the flask and heat for 30 min after refluxing begins (see note 2 in 7.2). Turn off the heat source and immediately add 50 ml of the petroleum spirit (5.5) (see notes 3 and 4 in 7.2) by cautiously pouring it down the condenser (disconnect the condenser if a mushroom-type is used).

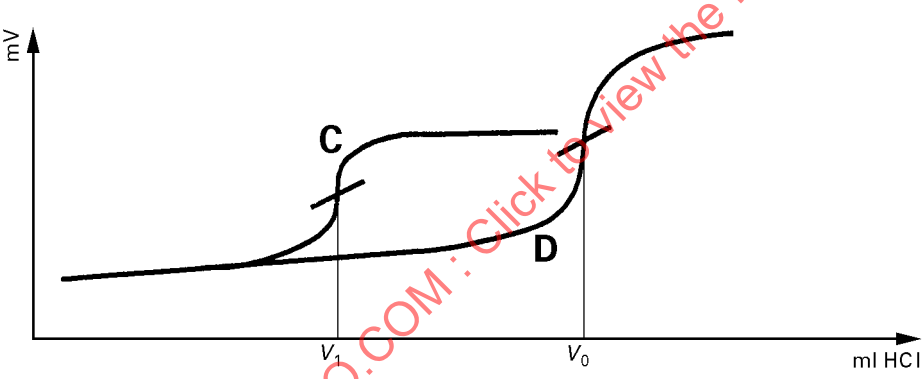
8.2.3 Titrate while hot, with no pre-addition of titrant, with the hydrochloric acid solution (5.3) as specified in 7.6 and 7.7. A complete titration curve is illustrated in figure 2.

NOTE — The potential readings are fairly constant. The reading before addition of titrant is – 520 mV. The first inflection point is moderately sharp and takes place around – 300 mV. The second inflection is extremely sharp and takes place around 50 mV.



A Sample
B Blank

a) Using carbonate-containing alcoholic KOH



C Sample
D Blank

b) Using carbonate-free alcoholic KOH

Figure 2 — Typical titration curves

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9 Calculation

Calculate the saponification number, SN, in milligrams of KOH per gram, from the following equation:

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

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 of sample), as follows:

a) for electrical insulating oils: to the nearest 0,1;

b) for saponification numbers below 50: to the nearest 0,5;

c) 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.

11.1 Repeatability limit

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 2,76 mg KOH/g in only one case in 20.

11.2 Reproducibility limit

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 10,4 mg KOH/g in only one case in 20.

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.

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Annex A
(normative)

Preparation, testing and maintenance of electrode system

A.1 Preparation of electrodes

A.1.1 If the calomel electrode is to be changed from non-aqueous to aqueous bridge, drain out the non-aqueous solution, wash with water and methanol, then rinse the outer jacket (salt bridge) several times with potassium chloride solution (5.8) and, finally, fill the outer jacket with this solution.

A.1.2 When using the sleeve-type electrode, carefully remove the ground-glass sleeve and thoroughly wipe both ground surfaces. Replace the sleeve loosely and allow a few drops of electrolyte to drain through to flush the ground-glass joint and to wet the ground surfaces thoroughly with electrolyte. Set the sleeve firmly in place, refill the outer jacket with potassium chloride solution (5.8), and rinse the electrode with chlorobenzene (5.10).

A.1.3 When in use, the electrolyte level in the calomel electrode shall be kept above that of the liquid in the titration beaker to prevent entry of contaminants into the salt bridge. When not in use, fill the calomel electrode with potassium chloride solution (5.8), leave the bung in the filling orifice, and immerse both electrodes in water, keeping the level of the electrolyte above that of the water.

A.2 Testing of electrodes

Test when new electrodes are installed and retest once a month thereafter by standardizing 10 ml of potassium hydroxide solution (5.2) using hydrochloric acid solution (5.3).

A.3 Maintenance of electrodes

A.3.1 Clean the glass electrode at least once every week during continual use, by immersion in cold chromosulfuric acid (see warning to 6.1) or an alternative strong oxidizing cleaner.

A.3.2 Drain the calomel electrode at least once each week and refill with fresh potassium chloride solution (5.8) as far as the filling hole. Ascertain that crystalline KCl is present. Maintain the electrolyte level in the calomel electrode above that of the liquid in the titration beaker at all times.

A.3.3 When not in use, immerse the lower halves of the electrodes in water. Do not allow them to remain immersed in titration solvent for any appreciable period of time between titrations. Although the electrodes are not extremely fragile, handle them with care at all times.

NOTE — Thorough cleaning of the electrodes, keeping the ground-glass joint free of foreign materials, and regular testing of the electrodes are very important in obtaining repeatable potentials, since contamination can introduce uncertain and erratic liquid contact potentials, resulting in non-repeatable results.

A.3.4 At the end of the blank titration, and between successive titrations, a thin film of potassium chloride (KCl) crystals coats the electrode and titrant delivery tip. Use a jet of water from a plastic squeeze bottle to remove it. Then rinse the electrode by immersion in a beaker full of water for a few seconds. Dry the electrode by blotting with a paper towel; do **not** rub the electrode.

A.3.5 At the end of a set of sample titrations, a mixture of potassium chloride (KCl) and of sample fractions coats the electrode and titrant delivery tip. Clean these by immersion in a solution of

50 ml of xylene;
38 ml of propan-2-ol;
38 ml of water.

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