

# Methods of test for petroleum and its products —

**Part 136: Determination of saponification  
number —**

**Section 136.2: Potentiometric titration  
method**

**(Identical with IP 136 Section 2/1999)**

ICS 75.080

# National foreword

This British Standard reproduces ISO 6293-2:1998 and implements it as the UK national standard. Together with BS 2000-136-136.1:1998, it supersedes BS 2000-136:1993 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

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**Further information is available from:**

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## Cross-references

The British Standards which implement international publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled “International Standards Correspondence Index”, or by using the “Find” facility of the BSI Standards Electronic Catalogue.

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## Summary of pages

This document comprises a front cover, an inside front cover, pages 136.2.1 to 136.2.7 and a back cover.

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# Petroleum products — Determination of saponification number —

## Part 2: Potentiometric titration method

**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,  $c(\text{KOH}) = 0,5 \text{ mol/l}$ ,** 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  $[\text{Ba}(\text{OH})_2]$  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.

### 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  $\pm 0,000 2 \text{ g}$  and dissolved in 100 ml  $\pm 0,01 \text{ ml}$  of carbon dioxide-free water, using phenolphthalein (5.6) to detect the end-point.

**5.3 Hydrochloric acid,  $c(\text{HCl}) = 0,5 \text{ mol/l}$ ,** 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.

### 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.

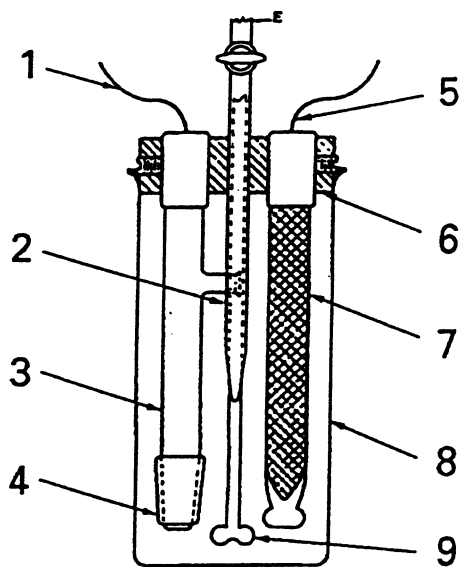
#### 6.2 Hotplate, heated by either electricity or steam.

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.



## 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

**6.5 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 x 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.

**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  $\pm 0,02$  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  $\pm 0,03$  ml of the alcoholic potassium hydroxide solution (5.2) and 25 ml  $\pm 1$  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 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

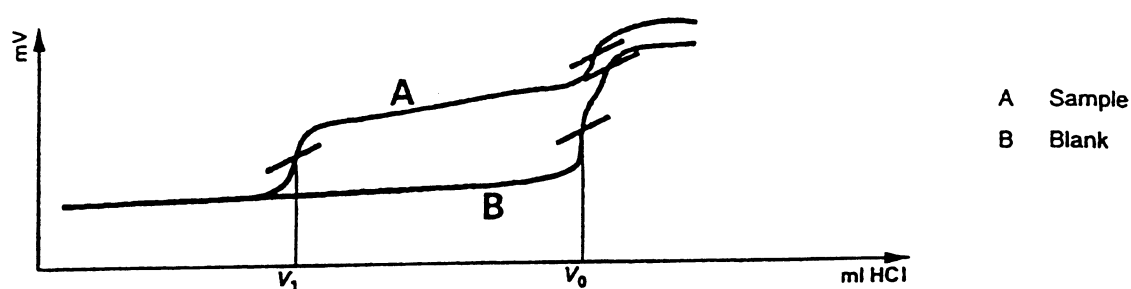
8.2.1 Weigh the test portion, to the nearest 0,01 g, into the conical flask (6.1).

Add 25 ml  $\pm$  1 ml of the butan-2-one (5.4), followed by 25 ml  $\pm$  0,03 ml of the alcoholic potassium hydroxide solution (5.2) measured from a burette or pipette (see note 1 in 7.2). Dissolve the difficult to dissolve samples first in 15 ml to 25 ml of xylene adding the butan-2-one.

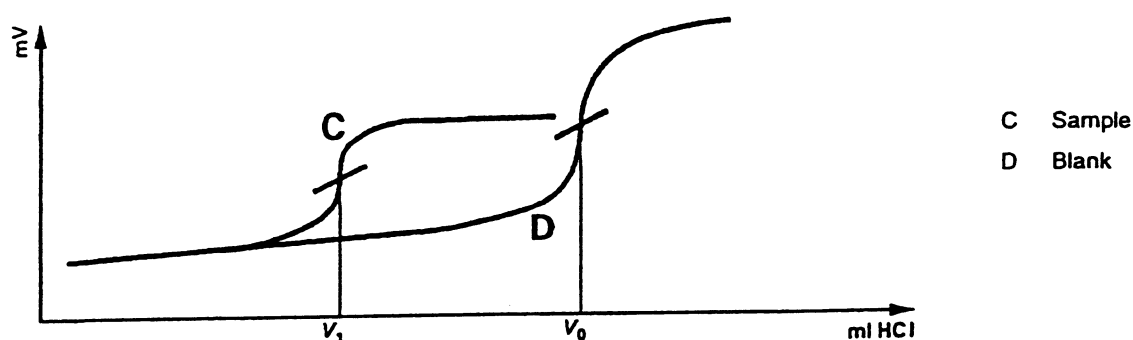
8.2.2 Connect the condenser to the flask and heat for 30 min after refluxing begins (see note 2 in 7.2). Turn off the heat source and immediately add 50 ml of the petroleum spirit (5.5) (see notes 3 and 4 in 7.2) by cautiously pouring it down the condenser (disconnect the condenser if a mushroom-type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



b) Using carbonate-free alcoholic KOH

Figure 2 — Typical titration curves

## 9 Calculation

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

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

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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