

Methods of test for

Petroleum and its products

**Part 1. Determination of acidity,
neutralization value - Colour indicator
titration method**

(Identical with IP 1/94)

Confirmed
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Foreword

This British Standard was published under the authority of the Materials and Chemicals Sector Board and comes into effect on 31 March 1995.

This British Standard supersedes BS 2000 : Part 1 : 1993, which is withdrawn.

BS 2000 comprises a series of test methods for petroleum and its products that are published by the Institute of Petroleum (IP) and have been accorded the status of a British Standard. Each method should be read in conjunction with the preliminary pages of 'IP Standard methods for analysis and testing of petroleum and related products' which gives details of the BSI/IP agreement for publication of the series, provides general information on safety precautions, sampling and other matters, and lists the methods published as Parts of BS 2000.

The numbering of the Parts of BS 2000 follows that of the corresponding methods published in 'IP Standard methods for analysis and testing of petroleum and related products'. Under the terms of the agreement between BSI and the Institute of Petroleum, the revised version of BS 2000 : Part 1 will be published by the IP (in 'Standard methods for analysis and testing of petroleum and related products' and as a separate publication). BS 2000 : Part 1 : 1995 is thus identical with IP 1/94.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

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The following BSI references
relate to the work of this standard:
Committee reference PTI/13
Draft for comment 94/108736 DC



Determination of acidity, neutralization value – Colour indicator titration method

This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations.

1 Scope

This standard describes methods for the determination of the acidity of unused lubricating oil (see note 3), fuel oil, and petrolatum.

Two alternative methods, A and B, are given for the determination of acidity. Method A is more suitable than method B for dark coloured oils and oils of viscosity higher than 120 mm²/s (cSt) at 40 °C and petrolatums. Method B is often preferred for pale coloured, low viscosity oils such as transformer oil. Method C is used to calculate organic acidity.

NOTE 1 Oils containing additives may give erroneous results.

NOTE 2 If there is elemental sulfur in solution, method A should be used, as method B may give rise to erroneous results due to interference with the indicator.

NOTE 3 The acidity of oxidized oils may also be determined by this method but precision has yet to be established.

NOTE 4 Results obtained by IP 139 are generally comparable with those obtained by method A of this standard, though with some oils, particularly used oil and those containing additives, there is a tendency for higher figures to be obtained.

2 Normative references

The following standard contains provisions which, through reference in this text, constitute provisions of this standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below.

IP 182/82 (88), BS 2000 : Part 182 : 1993, *Determination of inorganic acidity of petroleum products – Colour indicator titration method.*

3 Definitions

For the purposes of this standard, the following definitions apply.

3.1 acidity: A measure of the combined organic and inorganic acidity.

NOTE 5 This includes all substances which react with alcoholic potassium hydroxide under the conditions of the test.

3.2 inorganic acidity: A measure of the inorganic acid present in the sample as measured by IP 182.

3.3 organic acidity: A value obtained by deducting the inorganic acidity as determined by IP 182 from the acidity as determined by either method A or B of this standard.

4 Principle

Method A: The sample is dissolved in the solvent and the solution is titrated with 0,1 mol/l alkali.

Method B: The acidic products are extracted from the sample with ethanol and titrated with 0,1 mol/l alkali.

Method C: The organic acidity is calculated by subtracting the inorganic acidity as determined by IP 182 from the acidity as determined by either method A or B of this standard.

5 Reagents

Unless otherwise specified, use only reagents of recognized analytical grade.

5.1 Ethanol, 95 % (V/V), or IMS 66 op.

5.2 Potassium hydroxide standard solution (alcoholic, 0,1 mol/l). Either prepare a solution by the procedure given below (5.2.1) or use a commercially available potassium hydroxide solution of equivalent purity.

Standardize frequently enough to detect changes of 0,000 5 mol/l, preferably against 0,1 g to 0,15 g of pure potassium acid phthalate weighed to an accuracy of 0,000 2 g and dissolved in approximately 100 ml of carbon dioxide free water, using phenolphthalein to detect the end-point.

NOTE 6 Because of the relatively large coefficient of cubic expansion of organic liquids such as ethanol, standard alcoholic solutions should be standardized at temperatures close to those employed in the titrations of the sample.

5.2.1 Dissolve 6 g solid potassium hydroxide in 1 l of ethanol (5.1) and allow the solution to settle in a dark place. Decant, or filter the clear solution through glass wool, allow to stand for 24 h and standardize.

5.3 Hydrochloric acid, 0,1 mol/l.

5.4 Phenolphthalein solution, approximately 0.5% (m/V) in ethanol (5.1).

5.5 Alkali blue solution. Either prepare a solution by the procedure given below (5.5.1) or use a commercially available alkali blue 6B solution.

5.5.1 Extract 2 g of alkali blue 6B with ethanol (5.1) in a Soxhlet apparatus. Filter if necessary and dilute to 100 ml with ethanol. Add 3 ml of HCl (5.3) and after 24 h carry out an acid value test to check whether the indicator has been sufficiently sensitized by titrating with potassium hydroxide solution (5.2). If the colour does not change distinctly from blue to red, comparable to that of a 10% (m/V) solution of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), this indicates insufficient sensitization, and repeat the addition of HCl. Check again after a further 24 h. Continue until sensitization is satisfactory.

5.6 Toluene.

6 Apparatus

6.1 Burette, 10 ml capacity, Class A.

6.2 Conical flask, 250 ml capacity.

6.3 Air condenser.

NOTE 7 If using method B, use of conical flasks and air condensers with interconnecting ground glass joints is recommended.

6.4 Balance, sensitivity 0.000 2 g.

6.5 Hot plate or water bath.

Method A

7 Procedure

7.1 Unless the oil is known to be of low acidity, weigh to the nearest 0.01 g approximately 10 g of sample into a conical flask (6.2).

NOTE 8 If the oil is known to be of low acidity, a larger quantity of sample may be used.

7.2 To a mixture of 60 ml of toluene (5.6) and 40 ml of ethanol (5.1) in a separate flask add 2 ml \pm 1 ml of alkali blue solution (5.5). Neutralize the mixture with potassium hydroxide (5.2) to give a red colour that persists for at least 15 s and comparable to that of a 10% (m/V) solution of cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

7.3 Add the neutralized mixture to the sample, with swirling. If the mixture assumes a purple-blue colour after the sample is entirely dissolved, titrate it immediately with the potassium hydroxide (5.2) at a temperature not exceeding 30 °C. Consider the end-point has been reached when the purple-blue colour changes to the red colour of cobalt nitrate solution and persists for a minimum of 15 s or reverses with two drops of hydrochloric acid (5.3). Record the volume of the potassium hydroxide used.

Do not prolong the titration unnecessarily, as contamination with carbon dioxide appreciably affects the result.

NOTE 9 The effect of carbon dioxide can be obviated by the use of an atmosphere of nitrogen in the titration vessel and this procedure is recommended for referee purposes.

NOTE 10 Observation of the end-point in dark coloured solutions is made easier by the use of a narrow-bore glass tube as a stirrer. During the titration the tube can be used to withdraw temporarily a few drops of the solution for observation by transmitted light.

8 Calculation

Calculate the acidity, A , of the sample as milligrams of potassium hydroxide (KOH) per gram using the following equation:

$$A = \frac{56,1 MV}{W}$$

where

V is the volume of potassium hydroxide solution in millilitres;

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

W is the mass of sample in grams.

9 Expression of results

Report the result to the nearest 0,05 mg KOH/g of sample.

Method B

10 Procedure

10.1 Weigh to the nearest 0,01 g approximately 10 g of sample into a conical flask (6.2) (see note 8).

10.2 Add 1 ml of the phenolphthalein solution (5.4) to approximately 50 ml of ethanol (5.1) in a separate flask. Heat the mixture to between 40 °C and 50 °C and neutralize to a pale pink end-point with potassium hydroxide (5.2).

10.3 Add the neutralized ethanol to the sample. Insert the air condenser and heat the mixture to boiling on a water-bath or hot-plate. Allow to boil for 5 min and agitate by swirling to ensure extraction of the acids by the ethanol.

10.4 Add a further 1 ml of phenolphthalein solution (5.4), cool the mixture to between 40 °C and 50 °C and titrate it as quickly as possible with the potassium hydroxide solution (5.2) to a pale pink end-point (see note 10). Record the volume of the potassium hydroxide used.

11 Calculation

Calculate the acidity in accordance with clause 8.

12 Expression of result

Report the result to the nearest 0,05 mg KOH/g of sample.

Method C (organic acidity)**13 Procedure**

Determine the acidity of the sample in accordance with method A or B and the inorganic acidity in accordance with IP 182.

14 Calculation

Calculate the organic acidity of the sample by subtracting the inorganic acidity determined in accordance with IP 182 from the acidity determined in accordance with either method A or B.

15 Expression of result

Report the result to the nearest 0,05 mg KOH/g of sample.

16 Precision

The precision of the methods, as obtained by statistical examination of interlaboratory test results, is as shown in 16.1 and 16.2.

16.1 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 values shown in table 1 in only one case in 20.

Table 1 – Repeatability

	Method	Repeatability
Unused oils and petrolatums	A	0,1
	B	0,1
	C	0,1
Oxidized oils		Yet to be established

16.2 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 values shown in table 2 in only one case in 20.

Table 2 – Reproducibility

	Method	Reproducibility
Unused oils and petrolatums	A	0,1
	B	0,2
	C	0,1
Oxidized oils		Yet to be established

NOTE 11 Method C utilizes a result, obtained using IP 182, for which there is no precision. Therefore the precision given for method C is not based on current evaluation standards and can not be substantiated, but is included for guidance.

17 Test report

The test report shall contain at least the following information:

- the type and identification of the product tested;
- a reference to this standard and which method has been used, i.e. A, B or C;
- the result of the test (see clause 9, 12 or 15);
- any deviation, by agreement or otherwise, from the procedure specified;
- the date of the test.

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