

British Standard Methods of test for

Petroleum and its products

Part 139. Neutralization number of petroleum products and lubricants (colour indicator titration method)

(Identical with IP 139/65(81))

Méthodes d'essai du pétrole et des produits pétroliers

Partie 139. Indice de neutralisation des produits pétroliers et lubrifiants (méthode de titrage par indicateur coloré)

Verfahren zur Prüfung von Erdöl und Erdölprodukten

Teil 139. Neutralisationszahl von Erdölprodukten und Schmierstoffen (Farbindikator-Titration)

Foreword

BS 2000 comprises a series of test methods for petroleum and its products that have been published previously by the Institute of Petroleum (IP) and have been accorded the status of British Standards. Each method should be read in conjunction with BS 2000 : Part 0 'General introduction', which gives details of the BSI/IP agreement for publication of the series, lists more than 60 methods scheduled to be published in this way in 1982 and 1983, and provides general information on safety precautions, sampling and other matters.

The numbering of the other Parts follows that of the corresponding methods published in 'IP Standards for petroleum and its products, Part 1 Methods for analysis and testing'. BS 2000 : Part 139 is thus identical with IP 139/65 which was reapproved in 1981. Previous editions of this IP method were published in A5 format as BS 2834*, which has now been re-numbered and issued in the BS 2000 series and incorporates the editorial changes that have been made to the previous edition. It is intended to issue further revisions when necessary in line with any technical changes that may be made in subsequent editions of this IP method.

Caution. Attention is drawn to the safety precautions mentioned in Part 0 of this British Standard.

NOTE. The titles of the publications referred to in this Part of this British Standard are listed on the inside back cover.

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

WITHDRAWN

*Now withdrawn.

Method (identical with IP 139/65(81)¹)**SCOPE**

1. (a) This method is intended for the determination of acidic or basic constituents [Note 1] in petroleum products² and lubricants soluble or nearly soluble in mixtures of toluene and iso-propyl alcohol. It is applicable for the determination of acids or bases whose dissociation constants in water are larger than 10^{-9} ; extremely weak acids or bases whose dissociation constants are smaller than 10^{-9} do not interfere. Salts react if their hydrolysis constants are larger than 10^{-9} .

NOTE 1: In new and used oils, the constituents considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, and addition agents such as inhibitors and detergents. Similarly, constituents considered to have basic properties include organic and inorganic bases, amino compounds, salts of weak acids (soaps), basic salts of polyacidic bases, salts of heavy metals, and addition agents such as inhibitors and detergents.

NOTE 2: This method is not suitable for measuring the basic constituents of many basic additive-type lubricating oils. Method ASTM D664-IP 177, Test for Neutralization Number by Potentiometric Titration, can be used for this purpose.

NOTE to note 2. BS 2000 : Part 177 (formerly BS 4457) is identical with IP 177.

(b) This method may be used to indicate relative changes 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 or basic property that can be used to predict performance of an oil under service conditions. No general relationship between bearing corrosion and acid or base numbers is known.

NOTE 3: Oils, such as many cutting oils, rustproofing oils, and similar compounded oils, or excessively dark-coloured oils, that cannot be analysed by this method due to obscurity of the colour-indicator end point, can be analysed by Method ASTM D664-IP 177, Test for Neutralization Number of Potentiometric Titration Method. The acid or base numbers obtained by this colour-indicator method may or may not be numerically the same as those obtained by Method ASTM D664-IP 177, but they are generally of the same order of magnitude. Results obtained by the former ASTM Method D188 and ASTM Method D663, Test for Acid and Base Numbers of Petroleum Oils by Colour-Indicator Titration, are not comparable with and, particularly in the case of used oils, are appreciably lower than those obtained by this colour-indicator method.

NOTE to note 3. See note to note 2.

SUMMARY OF METHOD

2. To determine the total acid or strong base number, the sample is dissolved in a mixture of toluene and iso-propyl alcohol containing a small amount of water, and the resulting single-phase solution is titrated at room temperature with standard alcoholic base or alcoholic acid solution, respectively, to the end point indicated by the colour change of the added *p*-naphtholbenzein solution (orange in acid and green-brown in base). To determine the strong acid number, a separate portion of the sample is extracted with hot water and the aqueous extract is titrated with potassium hydroxide solution, using methyl orange as an indicator.

DEFINITIONS

3. (a) *Total Acid Number* – The quantity of base, expressed in milligrams of potassium hydroxide (KOH), that is required to titrate all acidic constituents present in 1 g of sample.

(b) *Strong Acid Number* – The quantity of base, expressed in milligrams of KOH, that is required to titrate the strong acid constituents present in 1 g of sample.

(c) *Strong Base Number* – The quantity of acid, expressed in terms of the equivalent number of milligrams of KOH, that is required to titrate the strong base constituents present in 1 g of sample.

APPARATUS

4. *Burette* – A 50 ml burette graduated in 0.1 ml subdivisions, or a 10 ml burette graduated in 0.05 ml subdivisions.

NOTE to clause 4. A burette complying with BS 846 is suitable.

¹ Under the standardization procedure of ASTM, this method is under the jurisdiction of the ASTM Committee D-2 on Petroleum Products and Lubricants.

In the IP, this method is under the jurisdiction of the Standardization Committee.

² Statements defining this test and its significance when applied to electrical insulating oils of mineral origin will be found in ASTM Methods D117, Testing Electrical Insulating Oils, *Annual Book of ASTM Standards*, Part 40.

PURITY OF REAGENTS AND MATERIALS

5. (a) *Purity of Reagents* – Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications for analytical reagents of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available or to other such recognized standards for reagent chemicals.³ Other grades may be used provided that it is known or first ascertained that the reagent is of sufficiently high quality to permit its use without lessening the accuracy of the determination.

(b) References to water shall be understood to mean distilled water.

NOTE to 5(b). Water complying with BS 3978 is suitable.

REAGENTS

6. (a) *Hydrochloric Acid Solution, Standard Alcoholic (0.1 N)* – Mix 9 ml of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1000 ml of anhydrous iso-propyl alcohol (containing less than 0.9% water). Standardize frequently enough to detect normality changes of 0.0005 [Note 4], preferably by electrometric titration of approx 8 ml (accurately measured) of the 0.1 N alcoholic KOH solution diluted with 125 ml of carbon dioxide-free water.

(b) *Methyl Orange Indicator Solution* – Dissolve 0.1 g of methyl orange in 100 ml of water.

(c) *p-Naphtholbenzein Indicator Solution* – The *p*-naphtholbenzein must meet the specifications given in the Appendix. Prepare a solution containing 10 g of *p*-naphtholbenzein⁴ per litre of titration solvent (Paragraph (e)).

(d) *Potassium Hydroxide Solution, Standard Alcoholic (0.1 N)* – Add 6 g of solid KOH to approx 1 litre of anhydrous iso-propyl alcohol (containing less than 0.9% water) in a 2 litre Erlenmeyer flask. Boil the mixture gently for 10 to 15 min, stirring to prevent the solids from forming a cake on the bottom. Add at least 2 g of barium hydroxide (Ba(OH)₂) and again boil gently for 5 to 10 min. Cool to room temperature, allow to stand for several hours, and filter the supernatant liquid through a fine sintered-glass or porcelain filtering funnel; avoid unnecessary exposure to carbon dioxide (CO₂) during filtration. 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 soda asbestos (Ascarite, Carbosorb, or Indocarb). Standardize frequently enough to detect changes of 0.0005 N [Note 4], preferably against pure potassium acid phthalate in about 100 ml of CO₂-free water, using phenolphthalein to detect the end point.

NOTE 4: To simplify calculations, both the standard KOH and HCl solutions may be adjusted so that 1.00 ml is equivalent to 5.00 mg of KOH. Sodium hydroxide (NaOH) and sulphuric acid (H₂SO₄) may be substituted for KOH and HCl, respectively.

(e) *Titration Solvent* – Add 500 ml of toluene and 5 ml of water to 495 ml of anhydrous iso-propyl alcohol.

NOTES to clause 6. *iso*Propyl alcohol complying with BS 1595 is suitable.

A conical flask complying with BS 2734 is suitable.

NOTE to 6(e). Toluene and *iso*Propyl alcohol, complying with BS 805 and BS 1595, respectively, are suitable.

PREPARATION OF USED OIL SAMPLES

7. (a) Strict observance of the sampling procedure described in Paragraph (b) is necessary, since the sediment itself is acidic or basic or has adsorbed acidic or basic material from the sample. Failure to obtain a representative sample causes serious errors.

(b) Heat the sample [Note 5] of used oil to 60 ± 5°C in the original container and agitate until all sediment is homogeneously suspended in the oil [Note 6]. If the original container is of opaque material, or if it is more than three-fourths full, transfer the entire sample to a clear glass bottle having a capacity at least one-third greater than the volume of the sample, and transfer all traces of sediment from the original container to the bottle by violent agitation of portions of the

³ 'Reagent Chemicals, American Chemical Society Specifications' (American Chemical Society, Washington, D.C., U.S.A.), or proprietary specifications for analytical grade chemicals.

For suggestions on the testing of reagents not listed by the American Chemical Society or by proprietary specifications, see 'Reagent Chemicals and Standards' by Joseph Rosin (Van Nostrand Inc., New York, N.Y., U.S.A.), the 'United States Pharmacopoeia,' or the 'British Pharmacopoeia.'

⁴ Solid *p*-naphtholbenzein conforming to the specifications given in the Appendix is available from Distillation Products Industries, Eastman Organic Chemicals Department, Rochester 3, N.Y.

NOTE to footnote 4. A list of suppliers of suitable *p*-naphtholbenzein indicator is available on application, enclosing a stamped addressed envelope, to Central Enquiries Section, British Standards Institution, 2 Park Street, London W1A 2BS.

sample in the original container. After complete suspension of all sediment, strain the sample or a convenient aliquot through a 100 mesh screen for the removal of large contaminating particles.

NOTE 5: When samples are visibly free of sediment, the heating procedure described in Paragraph (b) may be omitted.

NOTE 6: As used oil may change appreciably in storage, samples should be tested as soon as possible after removal from the lubricating system and the dates of sampling and testing should be noted.

PROCEDURE FOR TOTAL ACID NUMBER

8. (a) Into a 250 ml Erlenmeyer flask, introduce a weighed quantity of the sample as given in Table 1. Add 100 ml of the titration solvent and 0.5 ml of the indicator solution, and, without stoppering, swirl until the sample is entirely dissolved by the solvent. If the mixture assumes a yellow-orange colour, proceed as directed in Paragraph (b); if it becomes green or green-black, proceed as directed in Section 9.

NOTE to 7(b). A test sieve complying with BS 410 is suitable.

NOTE to 8(a). A conical flask complying with BS 2734 is suitable.

TABLE 1. Size of sample*

Total acid number or total base number	Size of sample, g	Sensitivity of weighing, g
<i>New or light-coloured oils</i>		
0.0 to 3.0	20.0 ± 2.0	0.05
Over 3.0 to 25.0	2.0 ± 0.2	0.01
Over 25.0 to 250.0	0.2 ± 0.02	0.001
<i>Used or dark-coloured oils</i>		
0.0 to 25.0	2.0 ± 0.2	0.01
Over 25.0 to 250.0	0.2 ± 0.02	0.001

* Light-coloured samples of low acid number permit the use of 20 g samples to obtain more precise results. The sample size for dark-coloured oils is limited to the quantity specified to minimize possible interference by the dark colour.

(b) Titrate immediately at a temperature below 30°C. Add 0.1 N KOH solution in increments and swirl to disperse the KOH as necessary. Shake vigorously near the end point, but avoid dissolving carbon dioxide (CO₂) in the solvent. (In the case of acidic oils, the orange colour changes to a green or green-brown as the end point is approached.) Consider the end point definite if the colour change [Note 7] persists for 15 sec or if it reverses with two drops of 0.1 N HCl.

NOTE 7: To observe the end point of dark-coloured oil, shake the flask vigorously to produce momentarily a slight foam when the colour change occurs as the last few drops of titrant are added and observe the titration under a white fluorescent lamp at bench-top level.

(c) *Blank* – Make a blank titration on 100 ml of the titration solvent and 0.5 ml of the indicator solution, adding 0.1 N KOH solution in 0.05 or 0.1 ml increments. Record the quantity of 0.1 N KOH solution required to reach the end point (orange to green).

NOTE 8: The titration solvent usually contains weak acid impurities which react with the strongly basic components of the sample. To correct the strong-base number for the sample, it is thus necessary to determine an *acid number* blank upon the solvent.

PROCEDURE FOR STRONG BASE NUMBER

9. (a) If the titration solvent containing the dissolved sample assumes a green or greenish-brown colour after the indicator is added (Section 8 (a)), carry out the titration as described in Section 8 (b), but use 0.1 N HCl and titrate until the green-brown colour changes to orange.

(b) *Blank* – Make a blank titration as directed in Section 8 (c) [Note 8].

PROCEDURE FOR STRONG ACID NUMBER

10. (a) Introduce approx 25 g of a representative sample, weighed to the nearest 0.1 g, into a 250 ml separatory funnel and add 100 ml of boiling water. Shake vigorously and drain the water phase, after separation, into a 500 ml casserole. Extract the sample twice more with 50 ml portions of boiling water, adding both extracts to the casserole. To the combined extracts add 0.1 ml of methyl orange indicator solution and, if the solution becomes pink or red, titrate with 0.1 N KOH solution until the solution becomes golden brown in colour. If the initial colour is neither pink nor red, report the strong-acid number as zero.

NOTE to 10(a). A separating funnel complying with BS 2021 is suitable.