

British Standard Methods of test for

Petroleum and its products

**Part 177. Neutralization number
by potentiometric titration**

(Identical with IP 177/83)

Méthodes d'essai du pétrole et des produits pétroliers

Partie 177. Indice de neutralisation par titrage potentiométrique

Verfahren zur Prüfung von Erdöl und Erdölprodukten

Teil 177. Neutralisationszahl durch potentiometrische Titration

WITHDRAWN

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, provides general information on safety precautions, sampling and other matters, and lists the methods scheduled for publication as Parts of BS 2000. When BS 2000 : Part 0 was first published in 1982, it included a list of more than 60 methods intended for publication in the first group of Parts of BS 2000; this Part was included in that list and it is envisaged that Part 0 will be revised from time to time to take account of the publication of additional methods.

The numbering of 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 177 is thus identical with IP 177/83.

BS 2000 : Part 177 was first published in 1983, when the method was identical with IP 177/64(79). As a result of discussions between the IP and the ASTM, IP 177 has since been revised and the current text of BS 2000 : Part 177 is identical with that of IP 177/83. The principal changes made since the previous edition include the addition of a 'significance' clause, restrictions on the storage life of buffer solutions, an additional reference to the use of automatic titrimeters for acid numbers and a modified 'precision' clause.

It is intended to revise this standard when necessary in line with changes that may be made in subsequent editions of the IP method.

Caution. Attention is drawn to the safety precautions mentioned in Part 0 of this British Standard, to the specific hazards indicated in 7.9, 7.10 and 7.11, and to the specific hazard associated with the use of toluene (7.15); toluene is a toxic volatile hydrocarbon which is absorbed by inhaling the vapour or through the skin by contact with the liquid. It should only be used in adequate ventilation and skin contact should be avoided.

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.

Method (identical with IP 177/83)¹**1. SCOPE**

1.1 This method describes procedures for the determination of acidic or basic constituents in petroleum products and lubricants [Note 1]. The method resolves these constituents into groups having weak-acid, strong-acid, weak-base, and strong-base ionization properties, provided the dissociation constants of the more strongly acidic or basic compounds are at least 1000 times that of the next weaker groups.

NOTE 1: In new and used oils, the constituents that may be considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, salts of ammonia and other weak bases, acid salts of polybasic acids, and addition agents such as inhibitors and detergents. Similarly, constituents that may be 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.

1.2. The method may be used to indicate relative changes that occur in an oil during use under oxidizing conditions regardless of the colour or other properties of the resulting oil [Note 2]. Although the titration is made under definite equilibrium conditions, the method is not intended to 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 number is known.

NOTE 2: A colour-indicator titration method is also available in ASTM D974-IP 139, Method of Test for Neutralization Number by Colour-Indicator Titration. The acid and base numbers obtained by the potentiometric method may or may not be numerically the same as those obtained by ASTM D974-IP 139 or equivalent colour indicator methods such as given in Federal Test Method Std No. 791 (a).

NOTE to note 2. BS 2000 : Part 139 is identical with IP 139.

2. APPLICABLE DOCUMENTS**2.1. ASTM Standards:**

D974 Test for Neutralization Number by Color-Indicator Titration.²

D1193 Specification for Reagent Water.³

D2896 Test for Total Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration.⁴

D3339 Test for Total Acid Number of Petroleum Products by Semi-Micro Color Indicator Titration.⁵

2.2. IP Standards:

IP 139 Test for Neutralization Number by Colour Indicator Titration.

IP 276 Test for Total Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration.

NOTE to clause 2. Reference to the documents referred to is not necessary for the purposes of this British Standard. See note to note 2.

3. DEFINITIONS

3.1. *Total Acid Number* – The quantity of base, expressed in milligrams of potassium hydroxide, that is required to neutralize all acidic constituents present in 1 g of sample.

3.2. *Strong Acid Number* – The quantity of base, expressed in milligrams of potassium hydroxide, that is required to neutralize the strong acid constituents present in 1 g of sample.

3.3. *Total Base Number* – The quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide that is required to neutralize all basic constituents present in 1 g of sample.

3.4. *Strong Base Number* – The quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide, that is required to neutralize the strong base constituents present in 1 g of sample.

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 *Annual Book of ASTM Standards*, Part 23.

³ *Annual Book of ASTM Standards*, Part 31.

⁴ *Annual Book of ASTM Standards*, Part 24.

⁵ *Annual Book of ASTM Standards*, Part 25.

4. SUMMARY OF METHOD

4.1. The sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide or hydrochloric acid solution, using a glass indicating electrode and a calomel reference electrode. The meter readings are plotted manually or automatically against the respective volumes of titrating solution and the end points are taken only at well defined inflections in the resulting curve. When no definite inflections are obtained, end points are taken at meter readings corresponding to those found for freshly prepared non-aqueous acidic and basic buffer solutions.

5. SIGNIFICANCE

5.1. New and used petroleum products may contain basic or acidic constituents that are present as additives or as degradation products formed during service, such as oxidation products. The relative amount of these materials can be determined by titrating with acids or bases. The acid number or base number is a measure of this amount of acidic or basic substances, respectively in the oil – always under the conditions of the test. The acid or base number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service. Any condemning limits must be empirically established.

Since a variety of oxidation products contribute to the acid number and organic acids vary widely in corrosion properties, the test cannot be used to predict corrosiveness of an oil under service conditions. No general correlation is known between acid number and the corrosive tendency of oils toward metals. Compounded engine oils can, and usually do, have both acid and base numbers in this test.

6. APPARATUS

6.1. *Potentiometric Titrimeter* – automatic recording or manual.

6.2. *Glass Indicating Electrode* – Calomel reference electrode.

6.3. *Stirrer, Buret, Stand, Titration Vessel* – as specified in Annex A1 are required. A typical cell assembly is shown in Fig. 1.

NOTE to 6.3. The spelling 'burette' is preferred to 'buret'.

NOTE 3: Combination electrodes, because of their slow response, have been found unsuitable for this method.

7. REAGENTS

7.1. Reagent grade chemicals shall be used. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society for analytical reagents or

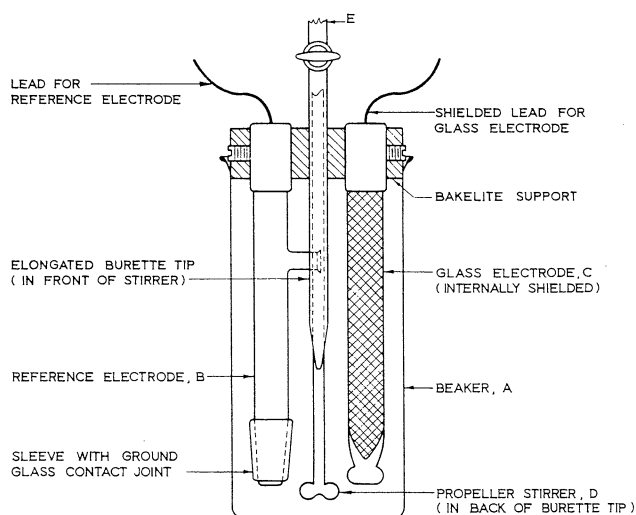


Fig. 1. Cell for potentiometric titration.

to other recognized standards for reagent chemicals.⁶ Other grades may be used provided it is known, or first ascertained, that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

7.2. Unless otherwise indicated, references to water shall be understood to mean distilled water.

7.3. *Buffer, Non-aqueous Acidic* – Add 10 ml of buffer stock solution A to 100 ml of titration solvent. Use within 1 h.

7.4. *Buffer, Non-aqueous Basic* – Add 10 ml of buffer stock solution B to 100 ml of titration solvent. Use within 1 h.

7.5. *Buffer Stock Solution A* – Accurately weigh 24.2 ± 0.1 g of 2,4,6-trimethyl pyridine (γ -collidine) and transfer to a 1 litre volumetric flask containing 100 ml of isopropyl alcohol. Using a 1 litre graduated cylinder, add to the flask, while continuously stirring its contents, $150/N_1 \pm 5$ ml of 0.2 N alcoholic HCl solution (N_1 being the exact normality of the HCl solution found by standardization). Dilute to the 1000 ml mark with isopropyl alcohol, and mix thoroughly. Use within 2 weeks.

7.6. *Buffer Stock Solution B* – Accurately weigh 27.8 ± 0.1 g of *m*-nitrophenol and transfer to a 1 litre volumetric flask containing 100 ml of isopropyl alcohol. Using a 250 ml graduated cylinder, add to the flask while continuously stirring its contents, $50/N_2 \pm 1$ ml of 0.2 N alcoholic KOH solution (N_2 being the exact normality of the KOH solution found by standardization). Dilute to the 1000 ml mark with iso-propyl alcohol, and mix thoroughly. Use within 2 weeks.

7.7. *Hydrochloric Acid Solution, Standard Alcoholic (0.1 N)* – Mix 9 ml of hydrochloric acid (HCl, rel d 1.19) with 1 litre of anhydrous isopropyl alcohol. Standardize frequently enough to detect normality changes of 0.0005 by potentiometric titration of approximately 8 ml (accurately measured) of the 0.1 N alcoholic KOH solution diluted with 125 ml of CO₂-free water.

7.8. *Hydrochloric Acid Solution, Standard Alcoholic (0.2 N)* – Prepare and standardize as directed in 7.7., but use 18 ml of HCl (rel d 1.19).

7.9. *Isopropyl Alcohol, Anhydrous*, (less than 0.1% H₂O). If adequately dry reagent cannot be procured, it can be dried by distillation through a multiple plate column, discarding the first 5% of material distilling overhead and using the 95% remaining. Also drying may be accomplished using molecular sieves such as Linde type 4A, by passing the solvent upward through a molecular sieve column using 1 part of molecular sieve per ten parts of solvent.

CAUTION: *Isopropyl alcohol is flammable. Use in adequate ventilation. Avoid prolonged breathing of vapour or mist spray. Avoid contact with eyes and skin.*

7.10. 2,4,6 Trimethylpyridine (γ -Collidine) (mol wt 121.18) – conforming to the following requirements:

Boiling range	168–170°C
Refractive index n_D^{20}	1.4982 ± 0.0005
Colour	colourless

Store the reagent over activated alumina and keep in a brown glass bottle.

CAUTION: *2,4,6 Trimethylpyridine (γ -Collidine) is hazardous if swallowed, breathed or spilled on skin or eyes. Wear chemical safety goggles, neoprene or rubber gloves and apron. Use only in a well-ventilated hood; or wear an approved respirator for organic vapour or a supplied-air respirator. Do not take internally.*

7.11. *m*-Nitrophenol (mol wt 139.11) – conforming to the following requirements:

Melting point	96–97°C
Colour	pale yellow

Store the reagent in a brown glass bottle.

CAUTION: *m*-Nitrophenol may be hazardous if swallowed, breathed or spilled on skin or eyes. Wear chemical safety goggles, neoprene or rubber gloves and apron. Use only in a well ventilated hood, or wear an approved respirator for organic vapour or a supplied-air respirator. Do not take internally.

7.12. *Potassium Chloride Electrolyte* – Prepare a saturated solution potassium chloride (KCl) in water.

NOTE to 7.2. Water complying with BS 3978 is suitable.

NOTES to 7.5.

NOTE 1. Isopropyl alcohol complying with BS 1595 is suitable.

NOTE 2. Volumetric flasks and graduated cylinders complying with BS 1792 and BS 604 respectively are suitable.

NOTES to 7.6. See notes 1 and 2 to 7.5. In line 6, the hyphenation of 'isopropyl' is in error.

NOTE to 7.7 See note 1 to 7.5.

NOTE to 7.9. See note 1 to 7.5.

NOTE to caution to 7.9. Details of fume cupboards, eye-protectors and gloves are given in DD 80, BS 2092 and BS 1651 respectively.

NOTE to caution to 7.10. See note to caution to 7.9.

NOTE to caution to 7.11. See note to caution to 7.9.

⁶ '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 (D. van Nostrand Inc., New York, N.Y., U.S.A.), the 'United States Pharmacopoeia,' or the 'British Pharmacopoeia'.

7.13. *Potassium Hydroxide Solution, Standard Alcoholic (0.1 N)* – Add 6 g of potassium hydroxide (KOH) to approximately 1 litre of anhydrous isopropyl alcohol. Boil gently for 10 min to effect solution. Allow the solution to stand for two days and then filter the supernatant liquid through a fine sintered-glass funnel. Store the solution in a chemically resistant bottle. Dispense in a manner such that the solution is protected from atmospheric carbon dioxide (CO₂) by means of a guard tube containing soda lime or soda asbestos (Ascarite, Carbosorb or Indecarb), and such that it does not come into contact with cork, rubber, or saponifiable stopcock grease. Standardize frequently enough to detect normality changes of 0.0005 by potentiometric titration of weighed quantities of potassium acid phthalate dissolved in CO₂-free water.

7.14. *Potassium Hydroxide Solution, Standard Alcoholic (0.2 N)* – Prepare, store, and standardize as directed in 7.13, but use 12 to 13 g of KOH to approximately 1 litre of isopropyl alcohol.

7.15. *Titration Solvent* – Add 500 ml of toluene and 5 ml of water to 495 ml of anhydrous isopropyl alcohol. The titration solvent should be made up in large quantities, and its blank value determined daily by titration prior to use.

NOTES to 7.15.

NOTE 1. Care should be exercised when using toluene (see caution in foreword). Toluene complying with BS 805 is suitable.

NOTE 2. See note 1 to 7.5.

8. PREPARATION OF ELECTRODE SYSTEM

8.1. *Maintenance of Electrodes* – Clean the glass electrode [Note 4] at frequent intervals (not less than once every week during continual use) by immersing in cold chromic acid cleaning solution. Drain the calomel electrode at least once each week and refill with fresh KCl electrolyte. Maintain the electrolyte level in the calomel electrode above that of the liquid in the titration beaker at all times. 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. While the electrodes are not extremely fragile, handle them carefully at all times.

CAUTION: *Chromic acid is potentially hazardous in contact with organic materials and is toxic and highly corrosive. If used wear approved full face shield and full-length protective clothing including gloves.*

NOTE to caution to 8.1 See note to caution to 7.9.

8.2. *Preparation of Electrodes* – Before and after using, wipe the glass electrode thoroughly with a clean cloth, or a soft absorbent tissue, and rinse with water. Wipe the calomel reference electrode with a cloth or tissue, 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 [Note 4]. Wet the ground surfaces thoroughly with electrolyte, set the sleeve firmly in place, and rinse the electrode with water. Prior to each titration, soak the prepared electrodes in water for at least 5 min immediately before use, and touch the tips of the electrodes with a dry cloth or tissue to remove the excess water.

8.3. *Testing of Electrodes* – Test the meter-electrode combination [Note 4] when first put into use, or when new electrodes are installed, and retest at intervals thereafter by dipping the electrodes into a well-stirred mixture of 100 ml of the titration solvent and 1.0 to 1.5 ml of 0.1 N alcoholic KOH solution. For the meter-electrode combination to be suitable for use, the potential between the electrodes should change by more than 0.480 V from the potential between the same electrodes when dipped in the non-aqueous acidic buffer solution [Note 5].

NOTE 4: Cleaning the electrodes thoroughly, keeping the ground-glass joint free of foreign materials, the regular testing of the electrodes are very important in obtaining reproducible potentials, since contamination may introduce uncertain, erratic, and unnoticeable liquid contact potentials.⁷ While this is of secondary importance when end points are chosen from inflexion points in the titration curve, it may be quite serious when end points are chosen at arbitrarily-fixed cell potentials.

NOTE 5: Considerably more sensitive electrodes are now available that will show a potential change of at least 0.590 V under these conditions, and their use is recommended.

⁷ For a detailed discussion of the need for care in preparation of the electrodes, see L. Lykken, P. Porter, H. D. Ruliffson, and F. D. Tuemmler, 'Potentiometric Determination of Acidity in Highly Coloured Oils,' *Industr. Engng Chem. Anal.*, 1944, **16**, 219–34.