

INTERNATIONAL STANDARD

**ISO
6618**

First edition
1987-12-15



INTERNATIONAL ORGANIZATION FOR STANDARDIZATION
ORGANISATION INTERNATIONALE DE NORMALISATION
МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

Petroleum products and lubricants — Neutralization number — Colour-indicator titration method

Produits pétroliers et lubrifiants — Indice de neutralisation — Méthode par titrage en présence d'indicateurs colorés

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6618 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Petroleum products and lubricants — Neutralization number — Colour-indicator titration method

1 Scope and field of application

1.1 This International Standard specifies a colour-indicator titration method for the determination of acidic or basic constituents in petroleum products and lubricants soluble in mixtures of toluene and isopropyl alcohol. It is applicable for the determination of acids or bases whose dissociation constants in water are greater than 10^{-9} ; extremely weak acids or bases whose dissociation constants are less than 10^{-9} do not interfere. Salts react if their hydrolysis constants are greater than 10^{-9} .

NOTES

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 or polyacidic bases, salts of heavy metals, and addition agents such as inhibitors and detergents.

2 This method is not suitable for measuring the basic constituents of many basic additive-type lubricating oils. ISO 6619 can be applied for this purpose.

1.2 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 — Oils, such as many cutting oils, rustproofing oils, and similar compounded oils, or excessively dark-coloured oils, that cannot be analysed by this method owing to obscurity of the colour-indicator end-point, can be analysed in accordance with ISO 6619. The acid or base numbers obtained by this colour-indicator method may or may not be numerically the same as those obtained by ISO 6619, but they are generally of the same order of magnitude.

2 Reference

ISO 6619, *Petroleum products and lubricants — Neutralization number — Potentiometric titration method.*¹⁾

3 Definitions

3.1 **acid number** : The quantity of base, expressed in milligrams of KOH per gram, that is required to titrate all acidic constituents present in 1 g of sample when titrated under prescribed conditions.

3.2 **strong acid number** : The quantity of base, expressed in milligrams of KOH per gram, that is required to titrate the strong acid constituents present in 1 g of sample when titrated under prescribed conditions.

3.3 **strong base number** : The quantity of acid, expressed in terms of the equivalent number of milligrams of KOH per gram, that is required to titrate the strong base constituents present in 1 g of sample when titrated under prescribed conditions.

4 Principle

To determine the acid number or strong base number, the test portion is dissolved in a mixture of toluene and isopropyl 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 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 with methyl orange as indicator.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.1 **Hydrochloric acid**, 0,1 mol/l standard volumetric alcoholic solution.

1) At present at the stage of draft.

5.1.1 Preparation

Mix 9 ml of concentrated hydrochloric acid (HCl, $\rho_{20} = 1,19$ g/ml) with 1 000 ml of anhydrous isopropyl alcohol (containing less than 0,9 % water).

5.1.2 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 0,1 mol/l alcoholic potassium hydroxide solution (5.4) diluted with 125 ml of carbon dioxide-free water.

5.2 Methyl orange indicator solution.

Dissolve 0,1 g of methyl orange in 100 ml of water.

5.3 *p*-Naphtholbenzein indicator solution, meeting the specifications given in annexes A and B.

5.4 Potassium hydroxide, 0,1 mol/l standard volumetric alcoholic solution.

5.4.1 Preparation

Add 6 g of solid KOH to approximately 1 000 ml of anhydrous isopropyl alcohol (containing less than 0,9 % water) in a 2 litre conical flask. Boil the mixture gently for 10 to 15 min, stirring to prevent solids from forming a cake on the bottom.

Add at least 2 g of barium hydroxide $[\text{Ba}(\text{OH})_2]$ and again boil gently for 5 to 10 min.

Allow to cool to room temperature, and then to stand for several hours. Filter the supernatant liquid through a fine sintered-glass or porcelain filtering funnel; avoid unnecessary exposure to carbon dioxide 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 non-fibrous soda silicate absorbent (Ascarite, Carbosorb, or Indecarb).

5.4.2 Standardization

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

NOTES

1 To simplify calculations, both the standard potassium hydroxide and hydrochloric acid solutions may be adjusted so that 1 ml is equivalent to 5 mg of KOH.

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

5.5 Titration solvent.

Add 500 ml of toluene and 5 ml of water to 495 ml of anhydrous isopropyl alcohol.

6 Apparatus

Ordinary laboratory apparatus and

6.1 Burette, capacity 50 ml, graduated in 0,1 ml subdivisions, or capacity 10 ml, graduated in 0,05 ml subdivisions.

7 Preparation of test sample of used oil

7.1 Strict observance of the sampling procedure is necessary, since sediment may be acidic or basic or may have absorbed acidic or basic material from the sample. Failure to obtain a representative test sample causes serious errors.

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

7.2 Heat the laboratory sample of used oil to 60 ± 5 °C in the original container and agitate until all of the sediment is homogeneously suspended in the oil. If the original container is a can, or if it is glass and more than three-quarters full, transfer the entire sample to a clear glass bottle having a capacity at least one-third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by violent agitation of portions of the sample in the original container.

NOTE — When laboratory samples are visibly free from sediment, the heating procedure described may be omitted.

7.3 After complete suspension of all sediment, strain the test sample or a convenient aliquot through a 100 mesh (0,149 mm aperture) screen to remove large contaminating particles.

8 Determination of acid number

8.1 Into a 250 ml conical flask, introduce the mass of test portion as given in table 1. Add 100 ml of the titration solvent (5.5) and 0,5 ml of the indicator solution (5.3) and, without stoppering, swirl until the test portion is entirely dissolved by the solvent. If the mixture assumes a yellow-orange colour, proceed as specified in 8.2; if it becomes green or green-black, proceed as specified in clause 9.

Table 1 — Mass of test portion¹⁾

Type of oil	Acid number or total base number	Mass of test portion g	Accuracy of weighing g
New or light-coloured	0 to 3	20 ± 2	0,05
	Over 3 to 25	2 ± 0,2	0,01
	Over 25 to 250	0,2 ± 0,02	0,001
Used or dark-coloured	0 to 25	2 ± 0,2	0,01
	Over 25 to 250	0,2 ± 0,02	0,001

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

8.2 Titrate immediately at a temperature below 30 °C. Add the potassium hydroxide solution (5.4) in increments and swirl to disperse the potassium hydroxide as necessary. Shake vigorously near the end-point, but avoid dissolving carbon dioxide 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 persists for 15 s or if it reverses on addition of 2 drops of the hydrochloric acid solution (5.1).

NOTE — 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.

8.3 Carry out a blank titration on 100 ml of the titration solvent and 0,5 ml of the indicator solution, adding the potassium hydroxide solution in 0,05 or 0,1 ml increments. Record the quantity of potassium hydroxide solution required to reach the end-point (orange to green).

9 Determination of strong base number

9.1 If the titration solvent (5.5) containing the dissolved test portion assumes a green or greenish-brown colour after the indicator is added (8.1), carry out the titration as specified in 8.2, but use the hydrochloric acid (5.1) and titrate until the green-brown colour changes to orange.

9.2 Carry out a blank titration as specified in 8.3.

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

10 Determination of strong acid number

10.1 Introduce approximately 25 g of a representative sample, weighed to within 0,05 g, into a 250 ml separating funnel, and add 100 ml of boiling water. Shake vigorously and, after phase separation, collect the aqueous phase in a 500 ml beaker. Make two new extractions from the test sample, each time with 50 ml of boiling water, and add the extracts obtained to the same beaker.

To the combined extracts add 0,1 ml of the methyl orange indicator solution (5.2) and, if the solution becomes pink or red, titrate with the potassium hydroxide solution (5.4) until the solution becomes golden brown in colour. If the initial colour is not pink or red, report the strong acid number as zero.

10.2 Into a 250 ml conical flask, introduce 200 ml of the boiling water from the same source. Add 0,1 ml of the methyl orange indicator solution (5.2). If the indicator colour is yellow-orange, titrate with the hydrochloric acid solution (5.1) to the same depth and shade of colour obtained in the titration of the test portion.

If the indicator colour is pink or red, titrate with the potassium hydroxide solution (5.4) to the same end-point as that used in the test portion titration.

11 Expression of results

Express the results as acid number, or strong acid number, or strong base number, as appropriate.

11.1 Method of calculation

11.1.1 The acid number, AN, expressed in milligrams of KOH per gram, is given by the formula

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

where

V_1 is the volume, in millilitres, of potassium hydroxide solution required for titration of the test portion;

V_0 is the volume, in millilitres, of potassium hydroxide solution required for titration of the blank solution;

c_{KOH} is the concentration, in moles per litre, of the standard volumetric potassium hydroxide solution;

m is the mass, in grams, of the test portion.

11.1.2 The strong acid number, SAN, expressed in milligrams of KOH per gram, is given by the formula in 11.1.2.1 or 11.1.2.2, as appropriate.

11.1.2.1 If the blank titration is made with acid :

$$SAN = \frac{(V_2 \times c_{KOH}) + (V_3 \times c_{HCl}) \times 56,1}{m}$$

where

V_2 is the volume, in millilitres, of potassium hydroxide solution required to titrate the water extract (10.1);

V_3 is the volume, in millilitres, of hydrochloric acid solution required to titrate the blank solution (10.2);

c_{KOH} is the concentration, in moles per litre, of the standard volumetric potassium hydroxide 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.

11.1.2.2 If the blank titration is made with base :

$$SAN = \frac{(V_2 - V_4) \times c_{KOH} \times 56,1}{m}$$

where

V_4 is the volume, in millilitres, of potassium hydroxide solution required to titrate the blank solution (10.2);

the other symbols have the meanings indicated in 11.1.2.1.

11.1.3 The strong base number, SBN, expressed in milligrams of KOH per gram, is given by the formula

$$SBN = \frac{(V_5 \times c_{HCl}) + (V_0 \times c_{KOH}) \times 56,1}{m}$$

where

V_5 is the volume, in millilitres, of standard volumetric hydrochloric acid solution required for titration of the test portion (clause 9);

the other symbols have the meanings indicated in 11.1.1 and 11.1.2.1.

11.2 Precision

The precision of the method, as obtained by statistical examination of inter-laboratory test results, is as shown below.

11.2.1 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 2 in only one case in 20.

Table 2 – Repeatability

Neutralization number	Repeatability
0 to 0,1	0,03
Over 0,1 to 0,5	0,05
Over 0,5 to 1	0,08
Over 1 to 2	0,12

11.2.2 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 3 in only one case in 20.

Table 3 – Reproducibility

Neutralization number	Reproducibility
0 to 0,1	0,04
Over 0,1 to 0,5	0,08
Over 0,5 to 2,0	15 % of the neutralization number level

NOTES

1 This precision statement applies only to new, light-coloured, straight mineral oils and new and used inhibited steam turbine oils. Insufficient data are available on other oils coming within the scope of this International Standard, so no precision statement is given for such oils.

2 The precision values do not apply to oils that are so highly coloured as to obscure the end-point colour change.

12 Test report

The test report shall contain at least the following information :

- the type and identification of the product tested;
- a reference to this International Standard;
- the result of the test (see 11.1);
- any deviation, by agreement or otherwise, from the procedure specified;
- the date of the test.

Annex A

Specification for *p*-naphtholbenzein

(This annex forms an integral part of the Standard.)

A.1 Appearance

Red amorphous powder.

A.2 Chlorides content

Less than 0,5 % (*m/m*).

A.3 Solubility

10 g shall dissolve completely in 1 litre of the titration solvent (5.5).

A.4 Minimum absorbance

Dissolve exactly 0,1 g of test portion in 250 ml of methanol. Make up 5 ml of this solution to 100 ml with pH 12 buffer (see A.5.5). This final dilution shall have a minimum absorbance of 1,2 when read at the 650 nm peak using a Beckman DU or alternative type spectrophotometer, 1 cm cells, and water as the blank.

A.5 pH range

A.5.1 The indicator shall turn to the first clear green at a relative pH of $11 \pm 0,5$ when tested by the method for the pH range of *p*-naphtholbenzein indicator as specified in annex B.

A.5.2 The indicator shall require not more than 0,5 ml of 0,01 mol/l potassium hydroxide solution above that for the blank to bring the indicator solution to the first clear green (see clause B.8).

A.5.3 The indicator shall require not more than 1,0 ml of 0,01 mol/l potassium hydroxide solution above that for the blank to bring the indicator solution to a blue colour.

A.5.4 The initial pHr of the indicator solution shall be at least as high as that of the blank.

A.5.5 The buffer is made by mixing 50 ml of 0,05 mol/l dibasic sodium phosphate solution with 26,9 ml of 0,1 mol/l sodium hydroxide solution.

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Annex B

Method for determining pHr range of *p*-naphtholbenzein indicator

(This annex forms an integral part of the Standard.)

B.1 Scope and field of application

This method is intended for determining the acceptability of *p*-naphtholbenzein indicator for use in accordance with this International Standard with regard to colour change over a pHr range.

B.2 Definition

pHr : An arbitrary term which expresses the relative hydrogen ion activity in the toluene-isopropyl alcohol medium in a manner similar to that in which the term pH expresses the actual hydrogen ion activity in aqueous solutions. For the purpose of this International Standard, the pHr acidity scale is defined by two standard buffer solutions which have been designated pHr 4 and pHr 11. The exact relation between pHr and the true pH of a toluene-isopropyl alcohol solution is not known and cannot be readily determined.

B.3 Principle

A prescribed amount of indicator is titrated electrometrically through the various colour changes with potassium hydroxide alcoholic solutions and results are plotted against meter readings converted to pHr units.

B.4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

B.4.1 Potassium hydroxide, 0,01 mol/l standard volumetric alcoholic solution.

B.4.2 Titration solvent.

Add 500 ml of toluene and 5 ml of water to 495 ml of anhydrous isopropyl alcohol.

Prepare the titration solvent in large quantities.

B.4.3 Acidic buffer solution (pHr = 4,0).

Prepare a stock solution in accordance with ISO 6619. Add 10 ml of buffer stock solution to 100 ml of titration solvent (B.4.2). Use the diluted solution within 1 h.

B.4.4 Alkaline buffer solution (pHr = 11,0).

Prepare a stock solution in accordance with ISO 6619. Add 10 ml of buffer stock solution to 100 ml of titration solvent (B.4.2). Use the diluted solution within 1 h.

B.4.5 Potassium chloride electrolyte.

Prepare a saturated solution of potassium chloride (KCl) in water.

B.5 Apparatus

Meter, glass electrode, calomel electrode, stirrer, beaker and stand, as specified in ISO 6619.

B.6 Preparation of electrode system

Prepare the electrode system in accordance with ISO 6619.

B.7 Standardization of apparatus

B.7.1 Prior to each test or series of tests, set the meter to read on the pH scale, insert the electrodes into a beaker containing acidic non-aqueous buffer solution (B.4.3) at a temperature of 25 ± 2 °C and stir the solution vigorously. When the pH meter reading becomes constant, adjust the asymmetry potential dial of the instrument so that the meter reads 4,0.

B.7.2 Remove the acidic buffer, clean the electrodes, and immerse them in water for several minutes. Dry the electrodes and insert them in a beaker containing alkaline non-aqueous buffer solution (B.4.4) at 25 ± 2 °C. When the pH meter reading has become steady, record the exact value.

If the reading is within 0,2 pH unit of 11,0, the initial acidity, pHr, of unknown solutions may be read directly from the dial of the meter.

If the reading is not within 0,2 pH unit of 11,0, prepare a correction graph as shown in the figure. Use the graph to convert pH meter readings to initial acidity, pHr.

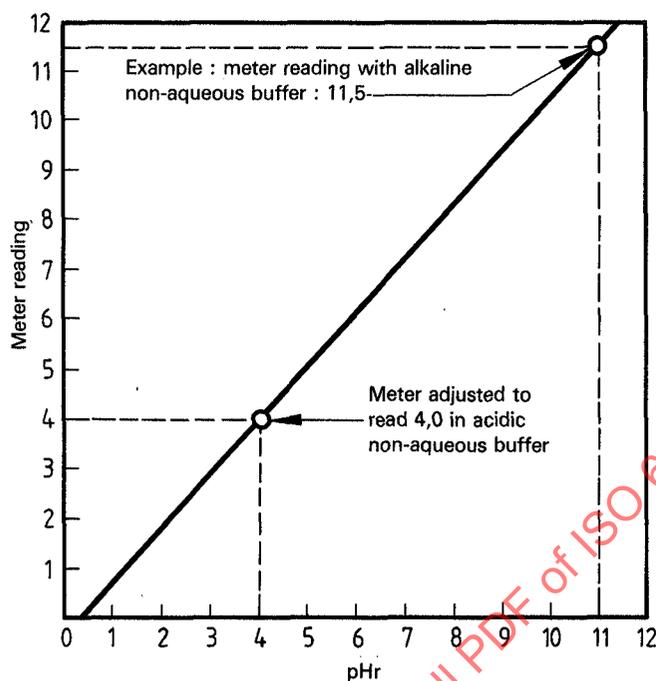


Figure — Example of calibration curve for conversion of pH meter readings to pHr

B.8 Procedure

B.8.1 Titrate 100 ml of titration solvent (B.4.2) with potassium hydroxide solution (B.4.1) until the meter indicates a pHr between 13 and 14.

B.8.2 Add 0,5 ml of the *p*-naphtholbenzein indicator solution under examination to a fresh portion of titration solvent and after cleaning the electrodes titrate with potassium hydroxide solution (B.4.1) until the meter indicates a pHr between 13 and 14.

B.8.3 During the titration, plot the volume of titrant against the pHr or meter reading and note on the curve the various colour changes at the corresponding pHr values.

NOTE — The following colour changes, in order, are intended as a guide :

- amber to olive green;
- olive green to clear green;
- clear green to bluish green;
- bluish green to blue.

B.8.4 Plot the results of the blank titration on the same paper as used for the indicator.

B.9 Expression of results

Subtract the volume of titrant used in the blank titration from that used for the indicator solution titration at the same pHr corresponding to the definite colour changes between 10 and 12 pHr.