

INTERNATIONAL STANDARD

ISO
6619

First edition
1988-12-01



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

Petroleum products and lubricants — Neutralization number — Potentiometric titration method

*Produits pétroliers et lubrifiants — Indice de neutralisation — Méthode par titrage
potentiométrique*

Reference number
ISO 6619:1988 (E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 6619 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Annex A of this International Standard is for information only.

Petroleum products and lubricants — Neutralization number — Potentiometric titration method

1 Scope

1.1 This International Standard specifies a method for the determination of acidic constituents in petroleum products and lubricants soluble or nearly soluble in mixtures of toluene and propan-2-ol. It is applicable for the determination of acids whose dissociation constants in water are larger than 10^{-9} ; extremely weak acids whose dissociation constants are smaller than 10^{-9} do not interfere. Salts react if their hydrolysis constants are larger than 10^{-9} .

NOTE — 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 base constituents, acid salts of polybasic acids, and additives such as inhibitors and detergents.

1.2 This 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. 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 number is known.

NOTE — A colour-indicator titration method is also available in ISO 6618 (see bibliography in annex A). The acid numbers obtained by the potentiometric method may or may not be numerically the same as those obtained by ISO 6618, but they are generally of the same order of magnitude.

1.3 New and used petroleum products may contain acidic constituents that are present as additives or as degradation products formed during service, such as oxidation products. The relative amounts of these materials can be determined by titrating with bases. The acid number is a measure of this

amount of acidic substances in the oil under the conditions of the test. The acid 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.

As a variety of oxidation products contribute to the acid number and the 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 an acid number in this test.

2 Definitions

For the purposes of this International Standard, the following definitions apply.

2.1 acid number: The quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate potentiometrically a test portion in a specified solvent from its initial meter reading to a meter reading corresponding to that obtained with a freshly prepared basic non-aqueous buffer solution or a well defined inflection point as specified in the standard.

2.2 strong acid number: The quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate potentiometrically a test portion in a specified solvent from its initial meter reading to a meter reading corresponding to that obtained with a freshly prepared acidic non-aqueous buffer solution or a well defined inflection point as specified in the standard.

3 Principle

The test portion is dissolved in a mixture of toluene and propan-2-ol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide 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 non-aqueous acidic and basic buffer solutions.

4 Reagents

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

4.1 Non-aqueous acidic buffer solution

Add 10 ml of buffer stock solution A (4.5) to 100 ml of titration solvent. Use within 1 h.

4.2 Non-aqueous basic buffer solution

Add 10 ml of buffer stock solution B (4.6) to 100 ml of titration solvent. Use within 1 h.

4.3 2,4,6-Trimethylpyridine (γ -Collidine) ($M_r = 121,18$), conforming to the following requirements:

Boiling range	168 to 170 °C
Refractive index, n_D^{20}	$1,498\ 2 \pm 0,000\ 5$
Colour	colourless

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

4.4 *m*-Nitrophenol ($M_r = 139,11$), conforming to the following requirements:

Melting point	96 to 97 °C
Colour	pale yellow

Store the reagent in a brown glass bottle.

4.5 Buffer stock solution A

Accurately weigh $24,2 \pm 0,1$ g of 2,4,6-trimethylpyridine (γ -collidine) and transfer to a 1-litre volumetric flask containing 100 ml of anhydrous propan-2-ol (4.9). Using a 1-litre graduated cylinder, add to the flask, while continuously stirring its

contents, $(150/c_1)$ ml ± 5 ml of 0,2 mol/l alcoholic HCl solution (4.8) (c_1 being the actual concentration of the HCl solution as found by standardization). Dilute to the 1 000 ml mark with propan-2-ol and mix thoroughly. Use within one month.

4.6 Buffer stock solution B

Accurately weigh $27,8 \pm 0,1$ g of *m*-nitrophenol and transfer to a 1-litre volumetric flask containing 100 ml of anhydrous propan-2-ol (4.9). Using a 500 ml graduated cylinder, add to the flask, while continuously stirring its contents, $(50/c_2)$ ml ± 1 ml of 0,2 mol/l alcoholic KOH solution (4.12) (c_2 being the actual concentration of the KOH solution as found by standardization). Dilute to the 1 000 ml mark with propan-2-ol and mix thoroughly. Use within one month.

4.7 Hydrochloric acid, standard volumetric alcoholic solution, $c(\text{HCl}) = 0,1$ mol/l.

Mix 9 ml of hydrochloric acid (HCl) ($\rho_{20} = 1,19$ g/ml) with 1 litre of anhydrous propan-2-ol (4.9). Standardize frequently enough to detect concentration changes of 0,000 5 mol/l by potentiometric titration of approximately 8 ml (accurately measured) of the 0,1 mol/l alcoholic KOH solution (4.11) diluted with 125 ml of carbon-dioxide-free water.

4.8 Hydrochloric acid, standard volumetric alcoholic solution, $c(\text{HCl}) = 0,2$ mol/l.

Prepare and standardize as directed in 4.7, but use 18 ml of HCl ($\rho_{20} = 1,19$ g/ml).

4.9 Propanol-2-ol, anhydrous [less than 0,1 % (*m/m*) H₂O].

If adequately dry reagent cannot be procured, it can be prepared by distillation through a multiple-plate column, discarding the first 10 % of material distilling overhead and the last 10 % remaining. Drying may also be accomplished using molecular sieves such as Linde type 4A¹⁾, passing the solvent upward through a molecular sieve column using one part of molecular sieve per ten parts of solvent.

4.10 Potassium chloride electrolyte

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

4.11 Potassium hydroxide, standard volumetric alcoholic solution, $c(\text{KOH}) = 0,1$ mol/l.

Add 6 g of potassium hydroxide (KOH) to approximately 1 litre of anhydrous propan-2-ol (4.9) in a 2-litre flask. Boil gently under reflux for 10 min and then shake to ensure it dissolves completely. Add at least 2 g of barium hydroxide [Ba(OH)₂] and again boil gently for 5 to 10 min.

1) Linde type 4A is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.