SLOVENSKI STANDARD
SIST EN 12634:1999

01-november-1999

Naftni proizvodi in maziva – Določevanje kislinskega števila – Metoda z nevodno potenciometrično titracijo

Petroleum products and lubricants - Determination of acid number - Non-aqueous potentiometric titration method

Mineralölerzeugnisse und Schmierstoffe - Bestimmung der Säurezahl - Potentiometrische Titration in nicht-wäßrigen Medien

Produits pétroliers et lubrifiants - Détermination de l'indice d'acide - Méthode par titrage potentiométrique en milieu non aqueux

Ta slovenski standard je istoveten z: **EN 12634:1998**

ICS:

75.080	Naftni proizvodi na splošno	Petroleum products in general
75.100	Maziva	Lubricants, industrial oils and related products

SIST EN 12634:1999 **en**

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 12634

October 1998

ICS 75.100

Descriptors: petroleum products, lubricants, additives, solvents, measurements, acid number, potentiometric methods

English version

Petroleum products and lubricants - Determination of acid number - Non-aqueous potentiometric titration method

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Ref. No. EN 12634:1998 E

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 19 "Petroleum products, lubricants and related products", the secretariat of which is held by NNI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 1999, and conflicting national standards shall be withdrawn at the latest by April 1999.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

In this standard annexes A and B are normative and annex C is informative.

Introduction

This potentiometric method in non-aqueous medium was developed because of the apparent need especially for industrial oils to be able to discriminate between strong, medium and weak acidic constituents and to follow the ageing process during use. The main advantage of the non-aqueous titration in contrast to a water containing one (e.g. ISO 6619[1]) is given by definitive inflection points.

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[1] ISO 6619 Petroleum products and lubricants - Neutralization number - Potentiometric titration method

1. Scope

This European Standard specifies a method for determination of acid number by potentiometric titration, of lubricating oils and additives soluble in mixtures of propan-2-ol, dimethylsulfoxide and toluene. It is applicable in the range 0,1 mg KOH/g to 250 mg KOH/g, and to unused and used lubricating oils and additives.

In the case of engine oils, used engine oils and oils with a high polymer content, e.g. viscosity index improvers, precision will be poor as the electrode performance will be impaired, and the application of this method is not recommended. Precision data are only valid for industrial oils and related products.

> NOTE : No direct conclusions can be drawn from the content of the acidic constituents on the suitability of lubricants for specific applications, and it is not possible to rate comparatively the quality of lubricants and additives on the basis of the quantity of acidic components.

WARNING. The use of this standard may involve hazardous materials, operations and equipment. 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 to determine the applicability of regulatory limitations prior to use.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are cited hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references, the latest edition of the publication referred to applies.

EN ISO 3696	Water for analytical laboratory use - Specification and test methods (ISO 3696:1987)
ISO 385-1	Laboratory glassware - Burettes - Part 1: General requirements
ISO 3170	Petroleum liquids - Manual sampling
ISO 3171	Petroleum liquids - Automatic pipeline sampling
ISO 3819	Laboratory glassware - Beakers

3 Definition

For the purposes of this standard, the following definition applies:

3.1 acid number

quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate potentiometrically the acidic constituents present in a test portion in a specified solvent to a defined end-point, i.e. the last inflection point.

4 Principle

A test portion is dissolved in a solvent mixture and titrated with alcoholic tetramethylammonium hydroxide solution. The titration is carried out potentiometrically by means of a glass electrode and a reference electrode; the end-point of the titration is taken as the last point of inflection of the titration curve (the equivalence point of the titration). Depending on the nature of the acidic constituents, one or more inflection points will occur, in decreasing order of acid strength.

5 Reagents

Use only reagents of recognized analytical grade, and water conforming to grade 3 of EN ISO 3696.

5.1 Methanol, [CH_3OH]

5.2 Ethanol, [C_2H_5OH]

5.3 Propan-2-ol, [C_3H_7OH]

5.4 Methylbenzene (Toluene), [$C_6H_5CH_3$]

5.5 Dimethylsulfoxide, [$(CH_3)_2SO$]

5.6 Solvent mixture, consisting of one part by volume of dimethylsulfoxide (see 5.5), eight parts by volume of propan-2-ol (see 5.3) and seven parts by volume of toluene (see 5.4).

5.7 Tetramethylammonium hydroxide (TMAH), [$(CH_3)_4NOH$]

Prepare a TMAH standard solution, approximately 0,1 mol/l, as follows.
Weigh, to the nearest 0,1 mg, approximately 9,1 g of TMAH, and dissolve in a mixture of three parts by volume of propan-2-ol (see 5.3) to one part by volume of methanol (see 5.1). Make up to 1 litre with the mixture and standardize the solution in accordance with annex A.
This standard solution is also commercially available.

5.8 Lithium chloride [LiCl] solution in ethanol, 3 mol/l

6 Apparatus

Usual laboratory apparatus and glassware, together with the following:

6.1 Titration apparatus

6.1.1 General, apparatus consisting of a titrimeter and stand, with a recording device, analog or digital, to measure the potentiometric output from the electrodes. The titrimeter, together with the electrodes, shall be protected from strong electrostatic fields by means of a suitable shield.

NOTE : Protection from electrostatic fields is ensured when the electrodes, any cable connections, or the titrimeter itself, are earthed and no permanent deflection occurs.

6.1.2 Titrimeter, capable of reading over the range -500 mV to +500 mV, with an operating accuracy of ±0,5 mV when operated with the electrodes specified in 6.1.3 and 6.1.4.

6.1.3 Glass electrode, with an electrical resistance of between 20 MΩ and 100 MΩ at 25 °C.

NOTE 1 : An electrical resistance of up to 500 MΩ can be used but sensitivity may be lost.

NOTE 2 : Low-temperature electrodes have been found to be particularly suitable.

6.1.4 Reference electrode, saturated calomel, or silver/silver chloride, with a sleeve and ground-glass joint diaphragm to contain the lithium chloride electrolyte bridge (see B.3).

Combined electrode systems, or reference electrodes, of alternative design may be used for routine analysis, but for referee purposes, the use of a sleeve-type reference electrode is required.

6.2 Stirrer, mechanical, electrical, or magnetic, with variable speed and with a propeller, paddle or stirring bar of chemically inert material. If an electrical stirrer is used, it shall be earthed (see note to 6.1.1).

6.3 Burette, manual or automatic, conforming to ISO 385-1. The capacity shall be either 5 ml or 10 ml, graduated in 0,05 ml divisions and calibrated with an accuracy of ± 0,02 ml.

6.4 Titration beaker, of borosilicate glass or a plastic material that is inert to the reagents used (see clause 5), and conforming to ISO 3819.

NOTE 1 : A tall-form beaker, with a capacity that ensures that the specified amount of titration solvent covers the electrodes, is preferred.

NOTE 2 : A 250 ml beaker is satisfactory, unless more than 50 g of sample is being analysed.

6.5 **Titration stand**, suitable for supporting the beaker, electrodes, stirrer and burette.

NOTE : An arrangement that allows removal of the beaker without disturbing the electrodes, burette and stirrer, is preferred.

7 Sampling

Unless otherwise specified in the commodity specification, samples shall be taken as described in ISO 3170 or ISO 3171, and/or in accordance with the requirements of national standards or regulations for the sampling of the product under test.

8 Sample preparation for used oils

As used oils can change appreciably in storage, samples shall be tested as soon as possible after removal from the lubricating system; the dates of sampling and testing shall be recorded in the test report.

Heat the sample to (60 ± 5) °C in the original container and agitate until any sediment is uniformly suspended in the oil. If the original container is a can, or made of 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 any traces of sediment from the original container to the bottle by violent agitation of portions of the sample in the original container. After complete suspension of any sediment, filter the laboratory sample, or a test portion, through a 150 µm wire mesh to remove large particles.

9 Apparatus preparation

The titration apparatus (see 6.1) shall be prepared in accordance with the manufacturer's instructions.

The reference electrode (see 6.1.4) requires careful attention to its maintenance and storage. Before use, the electrolyte bridge shall be filled or refilled with the lithium chloride solution (see 5.8). After use, the electrode shall be rinsed with the solvent mixture (see 5.6), with ethanol (see 5.2) and then with water, before preparation for storage. The preparation, maintenance and storage of the reference electrode shall be carried out in accordance with annex B.

The electrode system shall be checked for response characteristics by the procedure specified in annex B at an interval that does not exceed seven days prior to the analysis.

10 Procedure

10.1 Preliminary determination

If the approximate acid number of the sample is unknown, carry out a preliminary determination using the procedure given in 10.2, with the exception of titration rate, which can be increased to 0,6 ml/min, in order to assess the mass of sample required for the analysis. From this preliminary determination, select a mass of sample that will require (2 to 3) ml of TMAH solution (see 5.7).

NOTE : 10 g of unused oil, or 0,5 g of used oil, are recommended as test portion masses for the preliminary determination.

10.2 Determination

Carry out the determination in duplicate.

Weigh approximately, to the nearest 0,1 mg, the mass of test portion determined in 10.1 into the titration beaker (see 6.4). If the mass of the test portion is less than 50 g, add 150 ml of the solvent mixture (see 5.6), place the beaker on the titration stand, and start the stirrer. If the mass of the test portion is 50 g or more, use 200 ml of the solvent mixture. Mix thoroughly.

Turn off the stirrer and insert the glass (see 6.1.3) and reference (see 6.1.4) electrodes to a depth that ensures that they are adequately covered, but does not allow the stirred mixture to penetrate the electrolyte bridge of the reference electrode, i.e. the electrolyte level in the reference electrode shall be above that of the sample liquid in the titration vessel. Re-start the stirrer.

Insert the burette (see 6.3), filled with the TMAH standard solution (see 5.7), to a depth that places the tip just below the stirred liquid surface, and as far away from the electrodes as possible.

Titrate the test portion until the inflection point(s) is(are) passed, and the potential remains essentially constant. If an analogue recording output is used, titrate continuously at a rate of 0,2 ml/min to 0,3 ml/min. If a digital or manual output is used, titrate in discrete steps of 0,05 or 0,1 ml (around inflection points), and allow the potential to stabilize before further addition. For manual operation, plot a curve of potential against volume of TMAH standard solution added.

NOTE 1 : The final constant potential will be close to the potential of the TMAH standard solution (see 5.7).

Carry out a blank determination on 150 ml (or 200 ml) of solvent mixture (see 5.6) using the same procedure. If this value exceeds 0,3 ml, discard the solvent mixture and prepare a new batch.

NOTE 2 : The sensitivity of the inflection point can be enhanced by increasing the volume of solvent mixture.

10.3 Determination of the inflection point

NOTE: The occurence of more than one inflection point indicates the presence of acidic constituents of different acid strength.

10.3.1 Manual and digital output evaluation

Evaluate the inflection points of inflection by inspection of the plotted titration curve, and the last inflection point is defined by a change in potential of greater than 5 mV for an increment of TMAH addition.