BRITISH STANDARD

BS EN 62021-1:2003

Insulating liquids — Determination of acidity —

Part 1: Automatic potentiometric titration

The European Standard EN 62021-1:2003 has the status of a British Standard

ICS 29.040.10; 29.180

British Standards

National foreword

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The UK participation in its preparation was entrusted to Technical Committee GEL/10, Fluids for electrotechnical applications, which has the responsibility to:

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Liquides isolants -
Détermination de l'acidité
Partie 1: Titrage potentiométrique automatique
(CEI 62021-1:2003)

Isolierflüssigkeiten -
Bestimmung des Säuregehaltes
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(IEC 62021-1:2003)

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Foreword

The text of document 10/559/FDIS, future edition 1 of IEC 62021-1, prepared by IEC TC 10, Fluids for electrotechnical applications, was submitted to the IEC-CENELEC parallel vote and was approved by CENELEC as EN 62021-1 on 2003-09-01.

The following dates were fixed:

– latest date by which the EN has to be implemented at national level by publication of an identical national standard or by endorsement	(dop)	2004-06-01
– latest date by which the national standards conflicting with the EN have to be withdrawn	(dow)	2006-09-01

Annexes designated "normative" are part of the body of the standard.
In this standard, annex ZA is normative.
Annex ZA has been added by CENELEC.

Endorsement notice

The text of the International Standard IEC 62021-1:2003 was approved by CENELEC as a European Standard without any modification.

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INTRODUCTION

General caution

This International Standard does not purport to address all the safety problems associated with its use. It is the responsibility of the user of the standard to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

The insulating liquids which are the subject of this standard should be handled with due regard to personal hygiene. Direct contact with the eyes may cause slight irritation. In the case of eye contact, irrigation with copious quantities of clean running water should be carried out and medical advice sought.

Some of the procedures referenced in this standard involve the use of processes that could lead to a hazardous situation. Attention is drawn to the relevant standard for guidance.

Environment

This standard gives rise to mineral insulating oils, chemicals, used sample containers and fluid-contaminated solids. The disposal of these items should be carried out according to local regulations with regard to their impact on the environment. Every precaution should be taken to prevent the release into the environment of these oils.

INSULATING LIQUIDS –
DETERMINATION OF ACIDITY –

Part 1: Automatic potentiometric titration

1 Scope

This part of IEC 62021 describes the procedure for the determination of the acidity of unused and used electrical mineral insulating oils.

NOTE 1 In unused and used mineral insulating oils, the constituents that may be considered to have acidic characteristics include organic acids, phenolic compounds, some oxidation products, resins, organometallic salts and additives.

The method may be used to indicate relative changes that occur in a mineral insulating oil during use under oxidizing conditions regardless of the colour or other properties of the resulting mineral oil.

The acidity can be used in the quality control of unused mineral oil.

As a variety of oxidation products present in used mineral oil contribute to acidity and these products vary widely in their corrosion properties, the test cannot be used to predict corrosiveness of a mineral oil under service conditions.

NOTE 2 The acidity results obtained by this test method may or may not be numerically the same as those obtained by colorimetric methods, but they are generally of the same magnitude.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IEC 60475, *Method of sampling liquid dielectrics*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
acidity
quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate potentiometrically a test portion in a specified solvent to obtain a pH of 11,5

3.2
unused oil
mineral oil which has not been used in, or been in contact with, electrical equipment

4 Principle

The test portion is dissolved in solvent and titrated potentiometrically with alcoholic potassium hydroxide using a glass-indicating electrode and a reference electrode. The meter readings are plotted automatically against the respective volumes of titrant and the end-point is taken when the volume corresponds to a pH of 11,5. This was found to include all inflection points, with very little effect on the result from the rapid change in pH after the last inflection point. While use of inflection points is more accurate, it was found that measurement of weak inflection points was more instrument-dependent and gave poorer reproducibility.

5 Reagents and auxiliary products

5.1 Reagents

Only reagents of recognized analytical grade and de-ionized water or water of equivalent purity shall be used.

5.2 Titration reagent

Standard volumetric alcoholic solution 0,05 mol/l potassium hydroxide.

Add 3,0 g of potassium hydroxide to 1 000 ml ± 10 ml of 2-propanol. Boil gently for 10 min to effect solution. Cool and stopper the flask.

Allow the solution to stand in the dark for 2 days and then filter the supernatant liquid through a 5 μm membrane filter. Store in a suitable amber glass bottle.

The concentration of this solution is approximately 0,05 mol/l and shall be standardized as described in 10.1. For periodic tests on equipment in service, faster titration may be achieved by the use of 0,1 mol/l potassium hydroxide by agreement between the laboratory and the equipment owner, although this may result in poorer precision and detection limit.

Store in such a manner that the solution is protected from atmospheric carbon dioxide by means of a guard tube containing soda-lime absorbent and in such a way that it does not come into contact with cork, rubber or saponifiable stopcock grease.

Commercial alcoholic potassium hydroxide solution may be used, if necessary diluting to 0,05 mol/l with 2-propanol. This shall be standardized as described in 10.1.

5.3 Titration solvent

2-propanol (isopropanol, IPA).

5.4 Potassium hydrogen phthalate, primary standard

This should be dried before use for 2 h at 105 °C.

NOTE A 0,1 mol/l solution of hydrochloric acid in de-ionized water, prepared as in ISO 6619, may be used. Other acids may be used, provided they are certified against a primary standard.

5.5 Potassium chloride reference electrolyte

Prepare a solution of potassium chloride in de-ionized water at the concentration recommended by the electrode manufacturer. Commercially available solutions may be used where available.

5.6 Aqueous buffer solutions

Buffer solutions of suitable pH for calibration of electrodes, for example, pH 4, pH 7 and pH 11.

5.7 Cleaning solution

Weigh 8 g of ammonium peroxydisulphate into a glass beaker. Carefully add 100 ml of 98 % sulphuric acid and gently stir. Before use, the solution should be left overnight for the solid to dissolve completely.

WARNING – Ammonium peroxydisulphate is a strong oxidizing agent. Sulphuric acid is a strong corrosive agent. Handle carefully.

Commercially available cleaning solutions as recommended by the electrode manufacturer may be used.

6 Apparatus

6.1 Potentiometric titration apparatus

An automatic pH titrimeter capable of titrating to a fixed end-point using either variable or fixed titrant increments.

The instrument shall be protected from stray electrical fields so that no change of the reading is produced by touching any part of the system with a grounded lead.

An automatic burette with a dispensing accuracy of ±0,005 ml or better is required.

A reservoir for the titrating solution. It shall be fitted with a guard tube containing soda lime or other carbon dioxide absorbing material.

6.2 Glass indicating electrode

A glass electrode specifically designed for non-aqueous titrations is recommended.

The electrode shall be connected to the potentiometer by means of a suitably screened cable such that the resistance between the screening and the entire length of the electrical connection is greater than 50 000 MΩ.

6.3 Reference electrode

The electrode shall be made of glass and shall be provided with a movable joint in the form of a sleeve or plug to facilitate easy washing of the reference electrolyte cell. It is recommended that a double junction design is used and the electrolyte cells filled with potassium chloride electrolyte (see 5.5). The electrode shall be reserved for non-aqueous titrations.

NOTE Certain alternative electrode-electrolyte combinations have been found to give satisfactory results, although the precision using these alternatives has not been determined. Combined electrodes may be used provided they otherwise conform to this standard and have at least a similar speed of response.

6.4 Stirrer

The stirrer should have a variable speed and be fitted with a propeller, paddle or magnetic bar of chemically inert surface material. It shall be electrically grounded to avoid any change in the meter reading during the course of the titration.

6.5 Titration vessel

This should be as small as possible, sufficient to contain the solvent, sample, stirrer and electrodes and be inert to the reagents. Glass vessels are preferred to prevent build-up of electrostatic charge.

6.6 Titration stand

A suitable stand to support the beaker, electrodes, stirrer and burette.

7 Sampling

Samples shall be taken following the procedure given in IEC 60475.

Ensure that the test portion is representative by thoroughly mixing, as any sediment present may be acidic or have adsorbed acidic material from the liquid phase.

8 Preparation and maintenance of electrode system

Although electrodes are not particularly fragile they should be handled carefully at all times.

8.1 Preparation

Rinse the electrodes with 2-propanol and finally with de-ionized water.

Following each titration immerse the electrodes in de-ionized water to remove any surplus electrolyte adhering to the outside of the electrode and allow excess water to drain off. The immersion time should be sufficient to prevent any memory effects on subsequent titrations.

When in use, any plug that is present on the reference electrode should be removed and the electrolyte level in the electrode kept above that of liquid in the titration vessel to prevent entry of contaminants into the electrode.

8.2 Maintenance

8.2.1 Glass electrode

Clean the electrode weekly by immersing the tip in 0,1 mol/l hydrochloric acid for 12 h followed by washing with de-ionized water. If more aggressive cleaning is required, immerse the electrode tip in cleaning solution (see 5.7) for 5 min and follow this by thorough washing with de-ionized water. This treatment should be carried out on a monthly basis when the electrode is in regular use.

When not in use, immerse the lower half of the electrode in de-ionized water. Do not allow the electrode to dry out. If this occurs it may be possible to reactivate by immersing in cleaning solution (see 5.7) as detailed above.

8.2.2 Reference electrode

Drain and fill the electrode with potassium chloride electrolyte (see 5.5) at least once a week. When using the sleeve-type electrode, carefully remove the ground-glass sleeve and thoroughly wipe both ground-glass sleeve surfaces. Replace the sleeve loosely and allow a few drops of electrolyte to drain through to flush the ground-glass joint and to wet the ground surfaces thoroughly with electrolyte. Set the sleeve in place and refill with potassium chloride electrolyte (see 5.5).

When not in use, immerse the electrode in electrolyte (see 5.5) keeping the level of the electrolyte in the electrode above that of the immersion fluid level. The filling apertures should be covered during storage.

The electrode should be cleaned as necessary (at least weekly) by flushing with de-ionized water. Refill with potassium chloride electrolyte (see 5.5).

9 Calibration of apparatus

Determine the pH reading for the buffer solutions (see 5.6) on a daily basis. The value of the titration end-point of pH 11,5 is then extrapolated and must be entered into the instrumental programme.

The linearity and slope of the potentiometric titrator over the pH range 4 to 11 should comply with the electrode manufacturer’s tolerances.

Temperature correction shall be applied.

NOTE Owing to the significant effect of temperature on the pH of the buffer solutions (see 5.6), it is desirable to keep the temperature as close to the buffer manufacturer's calibration temperature as possible.

10 Procedure

Set up the apparatus in accordance with the manufacturer’s instructions.

Rinse and fill the burette with 0,05 mol/l (or 0,1 mol/l as in 5.2) alcoholic potassium hydroxide solution (see 5.2).

Standardize the 0,05 mol/l alcoholic potassium hydroxide solution regularly against potassium hydrogen phthalate (see 10.1).

10.1 Standardization of alcoholic potassium hydroxide solution

Standardize the alcoholic potassium hydroxide solution potentiometrically against 0,1 g to 0,16 g of the potassium hydrogen phthalate, weighed to an accuracy of 0,0002 g and dissolved in approximately 100 ml of carbon dioxide free water.

$$\text{Molarity} = \frac{1000 \times m \times p}{204{,}23 \times V} \qquad (1)$$

where

m is the mass of potassium hydrogen phthalate, in g;

p is the purity of potassium hydrogen phthalate;

204,23 is the molecular weight of potassium hydrogen phthalate;

V is the volume of alcoholic KOH solution (see 5.2) used to titrate the solution, in ml.

Alternatively, standard 0,1 mol/l acid may be used to standardize the alcoholic KOH (see note in 5.4).

$$\text{Molarity} = \frac{V_1 \times 0{,}1}{V_0} \tag{2}$$

where

V_1 is the volume of 0,1 mol/l standard acid used to titrate the solution, in ml;

V_0 is the volume of potassium hydroxide solution, in ml.

10.2 Blank titration

Perform a blank titration in duplicate as in 10.3, on 20 ml ± 0,1 ml of the solvent (see 5.3) daily and after changing to a fresh batch of solvent.

Blank titrations shall be continued until two consecutive titrations differ by no more than 0,005 ml, based on 20 ml of solvent and the mean of these is calculated as V_0 (see Clause 11).

Where a higher solvent volume than 20 ml is required because of apparatus constraints, the same volume of solvent shall be used for the sample titration.

High values may arise from carbon dioxide absorption or inherent 2-propanol acidity. If the blank value is greater than 0,06 ml (based on 20 ml of solvent), steps shall be taken to remove the cause of the high values.

10.3 Sample titration

Prepare the sample for titration as described in Clause 7 and weigh 5 g ± 0,1 g of the mineral oil to the nearest 0,01 g into the titration vessel. Add 20 ml ± 0,1 ml of titration solvent (see 5.3).

Place the titration vessel on the titration stand and stir the solution until the sample has dissolved and the pH reading is constant, taking care to limit the speed of stirring to avoid spattering and/or stirring air into the solution.

Carry out the titration with 0,05 mol/l (or 0,1 mol/l as in 5.2) potassium hydroxide, following the instrument manufacturer’s recommendations, to an end-point of pH 11,5 or higher if the instrument cannot be set for a dead-stop titration.

NOTE 1 Dynamic titrant addition is preferred to reduce the overall analysis time.

NOTE 2 When the titration time exceeds 15 min, it may be necessary to prevent carbon dioxide absorption by blanketing the solution with nitrogen.

On completion of the titration, record the burette reading V_1 (see Clause 11) at the pH reading of 11,5.

Rinse the electrodes and burette tip with titration solvent (see 5.3). Re-hydrate the glass electrode by immersing the bulb in de-ionized water (see 8.1) and allow excess water to drain off. Where oxidized oil is analysed, the electrode should be immersed in de-ionized water containing a few drops of hydrochloric acid, followed by rinsing in de-ionized water.

If further titrations are not to be carried out immediately, the electrodes shall be stored in the de-ionized water.

11 Calculation

Calculate the acidity to the nearest 0,01, expressed as mg KOH/g of oil using the following equation:

$$\text{Acidity} = \frac{(V_1 - V_0) \times M \times 56{,}1}{m} \qquad (3)$$

where

V_1 is the volume of alcoholic KOH solution (see 5.2) used to titrate the test portion, in ml;

V_0 is the volume of alcoholic KOH solution (see 5.2) used for blank titration, in ml;

M is the molarity of alcoholic KOH solution (see 5.2);

m is the mass of the test portion used, in g.

12 Precision

12.1 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 below only in one case in 20:

- unused oils: 6 % of the mean value;
- used oils: 12 % of the mean value.

NOTE The repeatability values for unused oils only apply where the result is significantly above the quantification limit, which has been established as 0,014 mg KOH/g oil.

12.2 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 below only in one case in 20:

- unused oils: 28 % of the mean value;
- used oils: 35 % of the mean value.

NOTE Repeatability and reproducibility limits were established in accordance with ISO 5725 for used oil. Those for unused oil have been taken from ISO 6619.

13 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 Clause 11) expressed to the nearest 0,01 mg KOH/g of oil.
- Any deviation, by agreement or otherwise, from the procedure specified.
- The date of the test.

Annex ZA
(normative)

Normative references to international publications with their corresponding European publications

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 listed 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 (including amendments).

NOTE When an international publication has been modified by common modifications, indicated by (mod), the relevant EN/HD applies.

Publication	Year	Title	EN/HD	Year
IEC 60475	- [1]	Method of sampling liquid dielectrics	-	-

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[1] Undated reference.

Bibliography

ISO 5725 (all parts), *Accuracy (trueness and precision) of measurement methods and results*

ISO 6619, *Petroleum products and lubricants – Neutralization number – Potentiometric titration method*

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