

English Version

Ethanol as a blending component for petrol -
Determination of total acidity - Colour indicator titration
method

Ethanol comme base de mélange à l'essence -
Détermination de l'acidité totale - Méthode de titrage
par indicateur coloré

Ethanol zur Verwendung als Blendkomponente in
Ottokraftstoff - Bestimmung der Gesamtsäurezahl -
Farbindikator-Titration

This European Standard was approved by CEN on 15 January 2025.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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European foreword

This document (EN 15491:2025) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

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of an identical text or by endorsement, at the latest by September 2025, and conflicting national standards shall be withdrawn at the latest by September 2025.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 15491:2021.

In comparison with the previous edition EN 15491:2021, the following technical modification has been made:

- sparging with nitrogen before titration has been added to 8.4 and sparging during the titration has been made mandatory for clarification to the user and for better comparison of the results. This has no effect on the method precision.

This document has been prepared under a standardization request addressed to CEN by the European Commission. The Standing Committee of the EFTA States subsequently approves these requests for its Member States.

Any feedback and questions on this document should be directed to the users’ national standards body. A complete listing of these bodies can be found on the CEN website.

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5 Reagents and materials

Use only reagents of recognized analytical grade and water complying with the requirements of grade 3 of EN ISO 3696.

5.1 Potassium hydrogen phthalate

5.2 Potassium hydroxide solution 0,01 mol/l, a solution prepared in accordance with 5.2.1 or a commercially available standardized potassium hydroxide solution of equivalent concentration and purity. The reagent shall be protected against carbon dioxide absorption and restandardized frequently enough to detect concentration changes of 0,000 5 mol/l.

5.2.1 Dissolve approximately 0,6 g potassium hydroxide in 1 l of water and standardize using potassium hydrogen phthalate in accordance with 5.2.2.

5.2.2 Dry a quantity of potassium hydrogen phthalate (5.1) in an oven at approximately 120 °C for approximately 2 h. Place in a desiccator and allow to cool. Weigh approximately 0,1 g to the nearest 0,1 mg into a 250 ml flask and record this mass. Add approximately 50 ml of carbon dioxide free water (5.5) and swirl to dissolve. Add 2 drops of phenolphthalein indicator solution (5.3) and using a 50 ml burette (6.5), titrate to neutral end point with the potassium hydroxide solution. Carry out a blank determination using the same volume of carbon dioxide free water (5.5). Calculate the concentration C , in moles per litre, of the potassium hydroxide solution from Formula (1):

$$C = \frac{1000m}{204,23(V_1 - V_0)} \quad (1)$$

where

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

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

V_0 is the volume, in millilitres, of potassium hydroxide used for the blank.

5.3 Phenolphthalein indicator solution, approximately 10 g/l

Weigh approximately 1 g of phenolphthalein into the 100 ml volumetric flask (6.1). Add approximately 20 ml of ethanol (5.4) and swirl until dissolved. Make up to 100 ml with ethanol.

5.4 Ethanol, approximately 95 % (V/V).

5.5 Carbon dioxide free water

NOTE A suitable way of preparing carbon dioxide free water is to place approximately 100 ml of water in a 250 ml conical flask (6.3), fitted with a standard ground glass joint, heated to boiling on either a hot plate or gas burner and boiled for 2 min to 3 min. The flask and its contents are removed from the heat, a soda-lime (5.6) filled guard tube (6.7) is inserted, and cooled to ambient temperature before use.

5.6 Soda lime, for the guard tube (optional).

5.7 Nitrogen, carbon dioxide free.

6 Apparatus

- 6.1 **Volumetric flask**, Class A, 100 ml capacity.
- 6.2 **Measuring cylinder**, 100 ml capacity.
- 6.3 **Conical flask**, glass, with standard ground glass joint, approximately 250 ml capacity.
- 6.4 **Burette**, Class A, 50 ml capacity.
- 6.5 **Burette**, Class A, 10 ml capacity and graduated in 0,05 ml, or less, subdivisions.
- 6.6 **Pipette**, Class A, 50 ml capacity.
- 6.7 **Glass guard tube**, with ground glass joint to fit the conical flask (6.3) (optional).
- 6.8 **Sparging system**, a gas delivery system suitable to deliver directly into the liquid sample, with an external pressure of 69 kPa (10 psi).

7 Sampling and sample handling

- 7.1 Unless otherwise specified, laboratory samples shall be obtained by the procedures described in EN ISO 3170.
- 7.2 Take care to minimize the uptake of atmospheric carbon dioxide during sampling and sample handling.

8 Procedure

- 8.1 Fill the 10 ml burette (6.5) with the potassium hydroxide solution (5.2).
- 8.2 Using the measuring cylinder (6.2) measure approximately 50 ml of carbon dioxide free water (5.5) into the conical flask (6.3). Add two drops of phenolphthalein solution (5.3). Titrate with the standardized potassium hydroxide solution (5.2) to a faint pink end point.
- 8.3 Using the pipette (6.6) add 50 ml of the test portion to the neutralized water. Stopper the flask and swirl to mix the test portion and the water.
- 8.4 Remove the stopper, sparge the solution with nitrogen for 5 min at a flowrate of 400 ml/min. \pm 20 ml/min. Maintain the nitrogen flow and titrate the mixture using the standardized potassium hydroxide to a faint pink end point.
- 8.5 If the density of the ethanol to be tested is not known, determine it, in g/ml, at 15 °C to two decimal places.

9 Calculation

Calculate the total acidity, A_s , as acetic acid, of the sample in % (m/m), using the following Formula (2):

$$A_s = \frac{VC \times 0,12}{\rho} \quad (2)$$

where

C is the concentration, in moles per litre, of potassium hydroxide solution, see Formula (1);

V is the volume, in millilitres, of potassium hydroxide solution required to neutralize 50 ml of test portion;

ρ is the density, in grams per millilitre, of the test portion at 15 °C.

10 Expression of results

Report the total acidity content of the sample to the nearest 0,001 % (m/m).

11 Precision

11.1 General

The precision given was derived from statistical analysis by EN ISO 4259:2006 [2] of the results of interlaboratory testing of a matrix of ethanol samples produced in Europe from biomaterials such as raw wine, molasses, pulp and corn.

NOTE 1 The interlaboratory testing and the statistical evaluation are detailed in Research Report IP 538 [3].

NOTE 2 The precision was later checked and confirmed by a further analysis following EN ISO 4259-1:2017 [4].

11.2 Repeatability, r

The difference between two independent results obtained using this method for test material considered to be the same in the same laboratory, by the same operator using the same equipment within short intervals of time, in the normal and correct operation of the method that is expected to be exceeded with a probability of 5 % due to random variation, conforms to the following:

$$r = 0,000\ 960\ 4$$

11.3 Reproducibility, R

The difference between two independent results obtained using this method for test material considered to be the same in different laboratories, where different laboratory means a different operator, different equipment, different geographic location, and under different supervisory control, in the normal and correct operation of the method that is expected to be exceeded with a probability of 5 % due to random variation, conforms to the following:

$$R = 0,001\ 370$$

12 Test report

The test report shall contain at least the following information:

- a) reference to this document and its year of publication, i.e. EN 15491:2025;
- b) type and complete identification of the product tested;
- c) result of the test (see Clause 10);
- d) any deviation, by agreement or otherwise, from the procedure specified;
- e) date of the test.

Bibliography

- [1] IP 538/06, *Determination of the total acidity of ethanol – Colour indicator titration method*. Available from the Energy Institute, 61 New Cavendish Street, London, W1G 7AR, UK
- [2] EN ISO 4259:2006, *Petroleum products — Determination and application of precision data in relation to methods of test (ISO 4259:2006)*
- [3] Research Report: IP 538/06, *Precision evaluation on IP 538, Determination of the total acidity of ethanol – Colour indicator titration method*. Available from the Energy Institute, 61 New Cavendish Street, London, W1G 7AR, UK
- [4] EN ISO 4259-1:2017, *Petroleum and related products — Precision of measurement methods and results — Part 1: Determination of precision data in relation to methods of test (ISO 4259-1:2017)*