



SLOVENSKI STANDARD SIST EN 15692:2021

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Nadomešča:
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Etanol kot komponenta za dodajanje motornemu bencinu - Določevanje vode - Metoda potenciometrične titracije po Karlu Fischerju

Ethanol as a blending component for gasoline - Determination of water content - Karl Fischer potentiometric titration method

Ethanol zur Verwendung als Blendkomponente in Ottokraftstoff - Bestimmung des Wassergehaltes - Potentiometrische Titration nach Karl Fischer

Ethanol comme base de mélange à l'essence - Détermination de la teneur en eau - Méthode de Karl Fischer par titrage potentiométrique

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Ethanol as a blending component for gasoline - Determination of water content - Karl Fischer potentiometric titration method

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Détermination de la teneur en eau - Méthode de Karl
Fischer par titrage potentiométrique

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Ottokraftstoff - Bestimmung des Wassergehaltes -
Potentiometrische Titration nach Karl Fischer

This European Standard was approved by CEN on 14 June 2021.

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COMITÉ EUROPÉEN DE NORMALISATION
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European foreword

This document (EN 15692:2021) 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of an identical text or by endorsement, at the latest by January 2022, and conflicting national standards shall be withdrawn at the latest by January 2022.

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 15692:2009.

In comparison with the previous edition, the following technical modifications have been made:

- The original document was prepared by CEN/TC 19’s Ethanol Task Force under its Working Group 21 and is based on ISO 760 [1]. It is developed as an alternative to EN 15489 [2], delivering a method more widely used in the alcohol and beverage industry environment.
- The test method has been revised in terms of its precision and scope. A second interlaboratory study (ILS) in 2010 [5] confirmed the application to automotive ethanol (E85) fuel. Use of the method over time, especially in proficiency testing programmes, gave questions around whether the precision in the original document. When CEN/TC 19/WG 36 was requested to study the ILS reports, the recalculated precision results did not reflect the published precision.
- The newly calculated precision is lower than the one published and the statistics allow introducing a constant reproducibility for the determination of water content in ethanol. The test method lower limit could remain at 0,05 % (whereas the lowest sample mean was 0,02 %). So the scope range has not been changed, but the precision calculations have.

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.

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

EN 15692:2021 (E)**1 Scope**

This document specifies a method for the direct determination of water in ethanol to be used as a blending component for petrol, as well as in automotive ethanol (E85) fuel.

This method is applicable in the range 0,05 % (*m/m*) to 0,54 % (*m/m*).

NOTE For the purposes of this document, the term “% (*m/m*)” is used to represent the mass fraction.

WARNING — Use of this document might involve hazardous materials, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

EN ISO 3170, *Petroleum liquids - Manual sampling (ISO 3170)*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

3 Terms and definitions

For the purposes of this document, the following term and definition apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <https://www.electropedia.org/>
- ISO Online browsing platform: available at <https://www.iso.org/obp>

3.1**water content**

content of water determined by potentiometric Karl Fischer procedure as given in this document

4 Principle

A weighed test portion is injected into the titration vessel of a potentiometric Karl Fischer apparatus. The water present is titrated to a potentiometric end point using Karl Fischer reagent. Iodine (I₂), with presence of anhydride sulfur (SO₂), of methanol (CH₃OH) and of an appropriate nitrogen base (RN), is introduced for the Karl Fischer reaction. Based on the stoichiometry of the reaction, one mole of iodine reacts with one mole of water.

The reaction can be expressed as follows:



5 Reagents and materials

Use only chemicals and reagents of recognized analytical grade.

5.1 Karl Fischer reagent, pyridine-free Karl Fischer (KF) reagent, containing iodine, sulfur dioxide and an odourless amine and with a nominal water equivalent content of either 2 mg or 5 mg water per ml equivalent.

The Karl Fisher reagent shall be standardized daily before use (see 8.1).

5.2 Titration solvent methanol, anhydrous methanol containing less than 0,05 % (*m/m*) of water.

5.3 Water, complying with grade 3 of EN ISO 3696.

6 Apparatus

6.1 Karl Fischer titrator, using a potentiometric end-point.

NOTE Karl Fischer titrators are commercially available and some of them automatically stop the titration at the end-point. Instructions for operation of these devices are provided by the manufacturer and are not described here. The method described in this document is using a titrator with a 5 ml burette.

6.2 Electrode platinum/platinum

6.3 Syringes

NOTE Needles with bores between 0,5 mm and 0,8 mm have been found suitable, such as syringe of single use with Luer connection, 5 ml or 10 ml capacity.

6.3.1 Syringe, of approximately 10 μ l capacity, fitted with a needle of sufficient length to enable the tip to reach under the surface of the liquid in the titration vessel when inserted through the inlet-port septum.

6.3.2 Syringe, of approximately 10 ml capacity, fitted with a needle of sufficient length to enable the tip to reach under the surface of the liquid in the titration vessel when inserted through the inlet-port septum.

6.4 Analytical balance, capable of weighing to the nearest 0,1 mg.

6.5 Automatic burette, of 5 ml or 10 ml capacity, protected from humidity by the use of a molecular sieve (6.6) at the top.

Although it is recommended that an automatic burette connected to a reservoir containing the KF reagent (5.1) is used, a burette, of approximately 5 ml capacity, fitted with a guard tube filled with molecular sieve (6.6) to prevent the ingress of moisture, may also be used.

6.6 Molecular sieve, granulometry proximally 1,6 mm to 2,5 mm, pore size close to 1 nm.

If required to be dried it shall be placed in an oven at proximally 140 °C for about 8 hours, then cooled in a desiccator to room temperature.

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7 Sampling and sample handling

- 7.1 Samples shall be taken as described in EN ISO 3170.
- 7.2 Take care to minimize the uptake of atmospheric moisture during sampling and sample handling.
- 7.3 Samples shall be shaken before used.
- 7.4 Samples shall be stored capped at room temperature in a dry place to avoid modification of water content.

NOTE The use of a glass bottle that can be sealed with a septum has been found suitable for sampling and sample handling. In such a case, a test portion of the sample can be taken through the septum with a syringe fitted with a needle.

8 Procedure

8.1 Standardization of the Karl Fischer reagent

8.1.1 Add sufficient of the titration solvent (5.2) to the clean, dry titration vessel (6.1) to cover the electrodes. Seal all openings to the vessel, start the magnetic stirrer and adjust for smooth stirring action. Turn on the indication circuit and add KF reagent (5.1) from the burette until the end point is reached.

Swirl the titration vessel to dry inside walls. Add more KF reagent if needed until a steady end point is reached and maintained for at least 15 s.

Repeat these swirling and titration steps until the vessels walls are dry.

8.1.2 Fill a 10 µl syringe (6.3.1) with pure water, taking care to eliminate air bubbles. Wipe the needle with a tissue to remove any residual water from its surface. Using the balance (6.4) weigh the syringe and the water and record the mass in mg (W_1).

8.1.3 Insert the needle of the syringe into the titration vessel via the inlet port septum. Ensure that the tip of the needle is below the surface of the titration solvent. Add the contents of the syringe to the titration solvent in the vessel which has been adjusted to its end point. Titrate the water with KF reagent until a steady end point is reached and maintained at least 15 s.

After adding water, do not shake the vessel.

8.1.4 Record, to the nearest 0,01 ml, the volume of titrant needed to reach the end point (T).

Reweigh the empty syringe and record the mass in mg (W_2).

8.1.5 To check the conformance of the KF reagent, calculate the water equivalence of KF reagent, use the following equation:

$$F = W / T \quad (1)$$

where

F is the water equivalence of the KF reagent, expressed in mg/ml;

W is the mass of water added in mg ($W_2 - W_1$);

T is the volume of titrant needed to reach the end point, expressed in ml (see 8.1.4).

8.1.6 Repeat the procedure specified in 8.1.1 to 8.1.5 to give a duplicate value.

8.1.7 If the variation between the two titrations is greater than 2 % relative, discard the contents of the titration vessel. Introduce a further portion of appropriate titration solvent into the vessel and repeat the standardization procedure starting from 8.1.1.

8.1.8 If the titrations for two further portions of water still vary by more than 2 % relative, it is likely that either the KF reagent and/or the titration solvent have aged. Replace these with fresh reagents and repeat the procedure starting from 8.1.1

8.1.9 Record the mean water equivalence value (\bar{W}).

8.2 Analysis

8.2.1 Add fresh titration solvent (5.2) to the clean, dry titration vessel (6.1) and titrate the solvent to the end point conditions as described in 8.1.1.

8.2.2 Dry the inside of a 10 ml syringe (6.3.2) by drawing the titration solvent up into the syringe and discharging back into the titration vessel. If the vessel contents become wet, add KF reagent (5.1) until the end point is maintained for at least 15 s without further addition of titrant.

Repeat this drying procedure until no further addition of KF reagent is necessary to maintain the end point state for at least 15 s (alternatively, oven-dried syringes, cooled in a desiccator may be used).

8.2.3 Immediately after mixing, use the dry syringe to withdraw at least three portions of the sample and discard as waste.

8.2.4 Immediately withdraw a 4 ml to 8 ml (depending on the expected water content) test portion of the sample, clean the needle with a paper tissue and weigh the syringe and contents to the nearest 0,1 mg.

Insert the needle of the syringe into the titration vessel via the inlet port septum, such that the needle is above the surface of the solvent, and discharge its contents.

Withdraw the needle of the syringe. Reseal the vessel if necessary to prevent leakage.

Weigh to the nearest 0,1 mg and record the mass, m_1 , of the sample test portion taken.

8.2.5 Titrate to the end point state, which shall be stable for at least 15 s. Do not shake the cell after addition of the sample.

8.2.6 Record, to the nearest 0,01 ml, the volume of titrant needed to reach the end point (V).

The solvent should be changed when the test portion content exceeds 2 g of sample per 15 ml of solvent or when 4 ml of titrant per 15 ml of solvent has been added to the titration vessel.

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9 Calculation

Calculate the water content of the sample, C_s , expressed in % (m/m), using the following equation:

$$C_s = \frac{F \times V}{m_1 \times 10} \quad (2)$$

where

m_1 is the mass of the test portion, expressed in grams (g) (see 8.2.4);

F is the mass of water in 1 ml of KF reagent, expressed in mg/ml (see 8.1.5);

V is the volume of titrant required to reach the end point titration, expressed in ml (see 8.2.6).

10 Expression of results

Report the water content of the sample rounded to the nearest 0,01 % (m/m).

11 Precision

11.1 General

The precision given was derived from statistical analysis by EN ISO 4259-1 [3] of the results of interlaboratory test results of 2005 of a matrix of ethanol samples produced in Europe from bio materials such as raw wine, molasses, pulp and corn, with test results in the range (0,048 8 to 0,541 8) % (m/m). In addition, a further interlaboratory test on automotive ethanol (E85) fuel samples with test results in the range (0,041 to 0,489) % (m/m) has been executed in 2010.

NOTE The interlaboratory testing and the statistical evaluation (including the re-examination) are detailed in research reports [4], [5] and [6].

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 with 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, can be calculated using the following function:

$$r = 0,002 * (X + 2,005) \quad (3)$$

where

X is the average of the two results being compared.

11.3 Reproducibility, R

The difference between two independent results, obtained 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, can be calculated using the following function:

$$R = 0,023 6 \quad (4)$$

NOTE In fact the reproducibility has been determined as $0,010 5*(X+2,005)$, but it has been decided to set it as a constant.