

English Version

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

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

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

This European Standard was approved by CEN on 19 March 2009.

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Foreword

This document (EN 15692:2009) 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of an identical text or by endorsement, at the latest by October 2009, and conflicting national standards shall be withdrawn at the latest by October 2009.

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

This 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.

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

1 Scope

This European standard specifies a method for the direct determination of water in ethanol to be used in gasoline blends. It is applicable in the range 0,05 % (m/m) to 0,54 % (m/m).

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

WARNING — 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 determine the applicability of regulatory limitations prior to use.

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.

EN ISO 3170, *Petroleum liquids – Manual sampling (ISO 3170:2004)*

EN ISO 3696, *Water for analytical laboratory use – Specification and test methods (ISO 3696:1987)*

3 Terms and definitions

For the purposes of this European Standard, the following term and definition applies.

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 reagent, containing iodine, sulfur dioxide and a 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 with a water content of less than 0,05 % (*m/m*).

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 µl 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 with an accuracy of 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.

NOTE Although it is recommended that an automatic burette connected to a reservoir containing the Karl Fischer reagent 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 dessicator to room temperature.

7 Sampling and sample handling

7.1 Samples shall be taken as described in EN ISO 3170.

7.2 Take care to minimise 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. 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*).

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.

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

$$F = W / T \tag{1}$$

where,

- F* is the water equivalence of the KF reagent, expressed in mg/ml;
- W* is the mass of water added in mg (see 8.1.2);
- 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 Karl Fischer 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.

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 dessicator 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 water content) test portion of the sample, clean the needle with a paper tissue and weight the syringe and contents to the nearest 0,1 mg.

Insert 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 syringe, reseal the vessel, reweigh 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) and the water equivalence of KF reagent (m_2).

NOTE 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.

9 Calculation

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

$$C_s = \frac{m_2 \times V}{m_1 \times 10} \quad (2)$$

where

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

m_2 is the mass of water in 1 ml of Karl Fischer reagent, expressed in mg/ml (see 8.2.6);

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 to the nearest 0,01 % (m/m).

11 Precision

11.1 General

The precision given was derived from statistical analysis by EN ISO 4259 [3] of the results of interlaboratory testing of a matrix of ethanol samples produced in Europe from bio materials such as raw wine, molasses, pulp and corn.

NOTE The interlaboratory testing and the statistical evaluation are detailed in a research report [4].

11.2 Repeatability, *r*

The difference between two 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 following value in only one case in twenty.

$$r = 0,006 X + 0,008$$

(3)

where

X is the average of results being compared.

11.3 Reproducibility, *R*

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 following value only in one case in twenty.

$$R = 0,02 X + 0,093$$

(4)

where

X is the average of results being compared.

12 Test report

The test report shall contain at least the following information:

- a) reference to this European Standard, i.e. EN 15692;
- b) type and complete identification of the product tested;
- c) result of the test (see 10);
- d) any deviation, by agreement or otherwise, from the procedure specified in this European Standard, or regarded as optional;
- e) details of any incidents which may have influenced the test results;
- f) date of the test.

Bibliography

- [1] ISO 760, *Determination of water - Karl Fischer method - General method*
- [2] EN 15489, *Ethanol as a blending component for petrol — Determination of water content — Karl Fischer coulometric titration method*
- [3] EN ISO 4259, *Petroleum products — Determination and application of precision data in relation to methods of test (ISO 4259:2006)*
- [4] *Precision Evaluations on determination of the water content of ethanol – Potentiometric Karl Fischer titration method*, research report, January 2006, available from UNGDA, 174 blvd Camélinat, 92247 MALAKOFF Cedex, France, www.ungda.org