SLOVENSKI STANDARD

SIST EN 15492:2012

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Nadomešča:

SIST EN 15492:2009

Etanol kot komponenta za dodajanje motornemu bencinu - Določevanje anorganskega klorida in sulfata - Ionska kromatografska metoda

Ethanol as a blending component for petrol - Determination of inorganic chloride and sulfate content - Ion chromatographic method

Ethanol zur Verwendung als Blendkomponente in Ottokraftstoff - Bestimmung des Gehaltes an anorganischem Chlor und Sulfat - Ionenchromatographie

Éthanol comme base de mélange à l'essence - Détermination de la teneur en chlorures minéraux et en sulfates - Méthode par chromatographie ionique

Ta slovenski standard je istoveten z: **EN 15492:2012**

ICS:

71.080.60	Alkoholi. Etri	Alcohols. Ethers
75.160.20	Tekoča goriva	Liquid fuels

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EUROPEAN STANDARD

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English Version

Ethanol as a blending component for petrol - Determination of inorganic chloride and sulfate content - Ion chromatographic method

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Ethanol zur Verwendung als Blendkomponente in Ottokraftstoff - Bestimmung des Gehaltes an anorganischem Chlor und Sulfat - Ionenchromatographie

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

Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (EN 15492:2012) 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of an identical text or by endorsement, at the latest by July 2012, and conflicting national standards shall be withdrawn at the latest by July 2012.

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 supersedes EN 15492:2008.

The method described in this document was originally based on a method from a European Regulation on wine [1]. This method has been developed and revised in 2008 to suit the needs as expressed in the ethanol specification (EN 15376:2011 [2]), also drafted by CEN/TC 19.

The precision and range of application for both inorganic chloride and sulfate have again been updated based on a second interlaboratory study done by CEN/TC 19/WG 27 on “Elemental analysis”. Small parts of the procedure have been updated according to laboratory practice and a density correction has been included in order to be able to report the result of the test in mass fraction.

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, Croatia, 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, Turkey and United Kingdom.

1 Scope

This European Standard specifies an ion chromatographic (IC) method for the determination of inorganic chloride content in ethanol from about 1 mg/kg to about 30 mg/kg and of sulfate content in ethanol from about 1 mg/kg to about 20 mg/kg.

NOTE Sulfate content can be determined from 0,5 mg/kg to 1,0 mg/kg. However, the precision was not established as no samples with sulfate content in this range were included in the interlaboratory test.

WARNING — Use of this method may involve hazardous equipment, materials and operations. This method does not purport to address to all of the safety problems associated with its use, but it is the responsibility of the user to search and 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 15486:2007, *Ethanol as a blending component for petrol — Determination of sulfur content — Ultraviolet fluorescence method*

EN ISO 1042, *Laboratory glassware — One-mark volumetric flasks (ISO 1042)*

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

EN ISO 3675, *Crude petroleum and liquid petroleum products — Laboratory determination of density — Hydrometer method (ISO 3675)*

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

EN ISO 12185, *Crude petroleum and petroleum products — Determination of density — Oscillating U-tube method (ISO 12185)*

3 Principle

A test portion of ethanol sample is evaporated on a water bath. The dry residue is dissolved in water. The chloride and sulfate ion contents are determined by comparing the peak area in the chromatogram of the aqueous solution of the test portion with the curve of the calibration standards.

The calibration standards are prepared from suitable compounds in aqueous solution.

4 Reagents

Use only reagents of recognized analytical grade, such as “Ionic Chromatography grade”, unless otherwise specified.

4.1 Sodium chloride (NaCl), molar mass 58,44 g/mol.

4.2 Sulfuric acid (H_2SO_4), aqueous solution at 0,1 mol/l. The concentration of sulfuric acid shall be verified by titration, or shall be certified in case of commercially available product.

4.3 Water, for analytical laboratory use, conforming to grade 2 of EN ISO 3696.

4.4 Eluent compounds

4.4.1 Sodium carbonate (Na_2CO_3), molar mass 105,99 g/mol.

4.4.2 Sodium hydrogen carbonate ($NaHCO_3$), molar mass 84,01 g/mol.

4.4.3 Potassium hydroxide (KOH), molar mass 56,11 g/mol.

4.5 Nitric acid (HNO_3) aqueous solution, $c(HNO_3) \approx 0,75$ mol/l.

Cautiously add 50 ml ± 2 ml of nitric acid (ρ = 1,40 g/ml) to 500 ml ± 10 ml water (4.3).

Mix and allow to cool to room temperature.

Make up to 1 000 ml in a volumetric flask (5.3) with water (4.3).

5 Apparatus

Before use, wash glassware (5.3) and evaporating dish (5.6) with nitric acid solution (4.5) and rinse thoroughly with water (4.3).

5.1 Ion chromatograph equipped with the following components.

5.1.1 Injection system, manual or automatic, with a sampling loop with minimum capacity of 25 µl.

5.1.2 Pumping system, capable of delivering mobile phase flows between 0,5 ml/min and 1,5 ml/min with a precision better than 5 %.

5.1.3 Chromatographic column, of which the following conditions have been found satisfactory:

Column	Type	anion exchange resin
	Dimension	4,0 mm × 250 mm
	Mesh size	9,0 µm
Eluent	Composition	1 mmol/l Na_2CO_3 + 4 mmol/l $NaHCO_3$
	Flow rate	1,0 ml/min

NOTE A 25 mmol/l KOH eluent may be used instead of the carbonate eluent.

It is also possible to use a precolumn (4,0 mm × 50,0 mm) with the same anion exchange resin and, if necessary, equipped with suppressors to remove interference from eluent. The thermal regulation of the system is not required, as the acceptable temperature of the column is in the range from 15 °C to 30 °C.

5.1.4 Conductivity detector, if necessary equipped with suppressor.

5.1.5 Integrator or computer, capable of measuring peak areas and retention times and correct the data according to the baseline of the chromatogram.

5.2 Balance, capable of weighing with an accuracy of 0,01 mg.

5.3 Glassware: 25 ml, 50 ml, 100 ml and 1 000 ml volumetric flasks, according to EN ISO 1042, and 25 ml and 50 ml graduated cylinders.

5.4 Graduated pipettes, of 1 ml and 5 ml capacity or variable volume automatic pipettes fitted with disposable polypropylene tips.

5.5 Warm water bath

NOTE In order to avoid potential external contamination, the warm water bath should be exempt of chloride and sulfates, as during the evaporation process water can potentially be mixed into a certain extent with the ethanol samples.

5.6 Evaporating dish, capacity 100 ml to 250 ml.

5.7 Desiccator, containing freshly activated silica gel (or equivalent desiccant) with moisture content indicator.

5.8 Oven, thermostatically controlled at (105 ± 2) °C.

6 Sampling

Unless otherwise specified, obtain samples in accordance with the procedures given in EN ISO 3170 and/or in accordance with the requirements of national standards or regulations for the sampling of the product under test.

High-density polyethylene containers shall be used. The containers shall be carefully cleaned and rinsed with water (4.3) to avoid contamination.

Samples should be analysed as soon as possible after removal from bulk supplies to prevent loss of ethanol.

7 Preparation of calibration solutions

7.1 Intermediate calibration solutions

7.1.1 Approximately 50 mg/l chloride solution. Weigh 82,4 mg of sodium chloride (4.1) in a 100 ml volumetric flask (5.3). Bring to the mark with water (4.3) and homogenise. Dilute this solution 1:10 with water (4.3) and homogenise.

7.1.2 Approximately 150 mg/l sulfate solution. Add 1,5 ml of sulfuric acid (4.2) in a 100 ml flask (5.3). Bring to the mark with water (4.3) and homogenise.

7.1.3 The actual concentration of chloride and sulfate used shall be known to calculate the concentration of each ion in the solution, as 50 mg/l and 150 mg/l only represent target concentrations.

NOTE Alternatively, commercially available stock calibration solutions may be used, provided that the solutions are traceable to primary stock solutions or Certified Reference Materials and are free from other analytes if single ion solutions are employed.

7.2 Calibration solutions

Dilute the intermediate calibration solutions (7.1) with water (4.3) in five volumetric flasks to obtain calibration solutions having the ion contents as given in Table 1.

Fresh solutions shall be prepared daily.

Table 1 — Ion contents for calibration solutions

Solution	**Sulfate** mg/l	**Chloride** mg/l
1 (blank)	0	0
2	1,0	2,0
3	2,0	5,0
4	5,0	10,0
5	10,0	20,0

8 Preparation of apparatus

8.1 Setting up the instrument

Since instruments from different manufacturers have different configurations and settings, it is difficult to specify an exact procedure. Follow the manufacturer's instructions for setting up the instrument with aqueous solutions.

8.2 Calibration

Inject a minimum of 25 µl (5.1.1) of each calibration solution (7.2) in the chromatograph and measure the areas of the peaks corresponding to chloride and sulfate ions. Carry out two measurements for each solution and calculate the mean of the peak areas corresponding to each ion.

Construct the calibration curve of chloride and the calibration curve of sulfate using the linear regression by plotting the peak area values against the values of the respective ion concentrations.

A chromatogram of a calibration solution containing 5 mg/l each of chloride and sulfate ions is shown in Figure 1.

NOTE If the plot of the peak area values against the ion concentrations is not linear (correlation coefficient R^2 less than 0,99) then the procedure should be inspected for errors and, if necessary, the calibration should be repeated starting from Clause 7.