SLOVENSKI STANDARD
SIST EN 15492:2008

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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 15492:2007**

ICS:

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

SIST EN 15492:2008 **en,fr,de**

EUROPEAN STANDARD

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ICS 75.160.20

English Version

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

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

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: rue de Stassart, 36 B-1050 Brussels

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Foreword

This document (EN 15492:2007) 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of an identical text or by endorsement, at the latest by June 2008, and conflicting national standards shall be withdrawn at the latest by June 2008.

The method described in this document is based on a method from a European Regulation on wine [1]. As need for measuring sulfate in ethanol emerged during the drafting of the ethanol specification [2], the method was re-evaluated beside the applicability for inorganic chloride content determination. It showed that the principle was applicable to measuring sulfate, but at the moment the precision is still under study. Therefore this document is published as an intermediate step, allowing further investigation of the method.

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 an ion chromatographic (IC) method for the determination of inorganic chloride and of sulfate content in ethanol. The precision of the method was established for chloride content from 4 mg/l to 30 mg/l. However, the precision of the method for sulfate content was not established yet.

NOTE Preliminary measurements showed that sulfate content can be determined from (4 to 10) mg/kg.

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 ISO 1042, *Laboratory glassware — One-mark volumetric flasks (ISO 1042:1998)*

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 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 “IC grade”, unless otherwise specified.

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

4.2 Sulfuric acid (H_2SO_4), solution at 0,1 mol/l, of which the concentration is verified by titration, or is certified in case of commercially available product.

4.3 Water, for analytical laboratory use, conforming to grade 3 of EN ISO 3696.

4.4 Eluent compounds

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

4.4.2 Sodium hydrogen-carbonate ($NaHCO_3$), MW 84,01 g/mol.

4.4.3 Potassium hydroxyde (KOH), MW 56,11 g/mol.

4.5 Nitric acid (HNO_3) 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 with water (4.3).

5 Apparatus

5.1 Ion chromatograph equipped with the following components:

5.1.1 Injection system with a sampling loop of 25 µl capacity.

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 chemical suppressor 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 and 100 ml volumetric flasks, according to EN ISO 1042, and 25 ml graduated cylinder.

Before use, wash all glassware with nitric acid solution (4.5) and rinse thoroughly with water (4.3).

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

5.5 Water bath

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.

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.

Alternatively, commercially available stock calibration solutions can be used, provided that the solutions are traceable to primary stock solutions or CRMs 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 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.

The 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* less than 0,99) then the procedure should be inspected for errors and, if necessary, the calibration should be repeated starting from Clause 7.

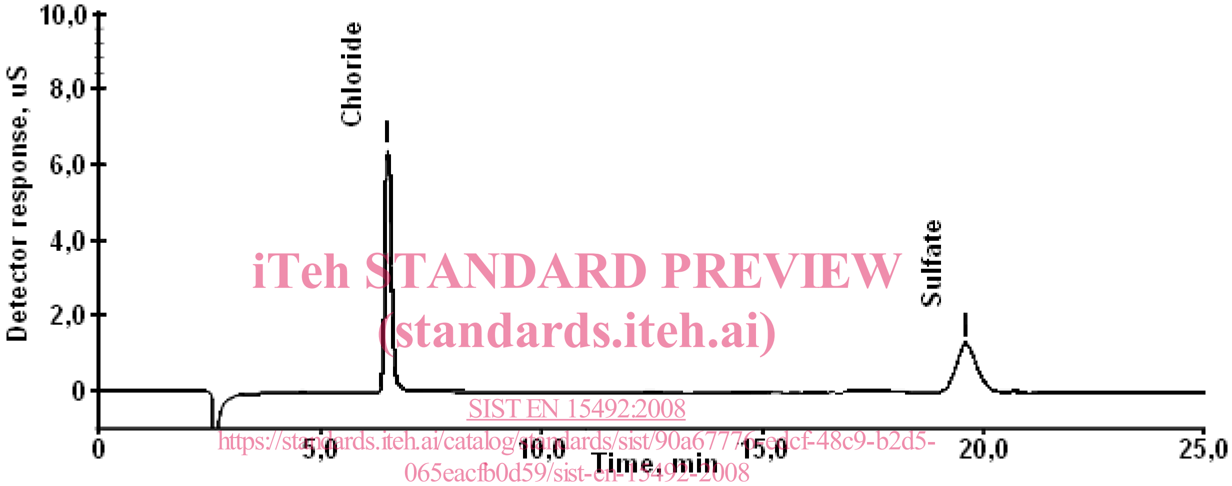

Figure 1 — Chromatogram of a solution

9 Procedure

9.1 Sample preparation

In order to avoid contamination, all sampling operations are carried out using polypropylene pipettes or automatic pipettes having disposable tips.

Manually shake the sample containers immediately prior to sampling of the test portions.

Add 25 ml (V_E) of test portion to the evaporating dish (5.6) using a graduated cylinder (5.3). Place the dish with sample on the boiling water bath (5.5) and allow to dry. Place the dish in the oven (5.8) at 105°C for 30 min and then transfer the dish in a desiccator (5.7). Allow the dish to cool for 30 min.

Add 5 ml of water (**Error! Reference source not found.**.3) to the dish and heat gently to dissolve the dry residue. Collect the treatment water in a 25 ml (V_S) volumetric flask. Repeat the treatment with water (**Error! Reference source not found.**.3) three times. Fill the flask to the mark with water (**Error! Reference source not found.**.3).

NOTE The time usually required to obtain the dry residue is about 2 h.