SLOVENSKI STANDARD

SIST EN 15487:2007

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Etanol kot komponenta za dodajanje motornemu bencinu - Določ evanje vsebnosti fosforja - Spektrometrijska metoda z amonijevim molibdatom

Ethanol as a blending component for petrol - Determination of phosphorus content - Ammonium molybdate spectrometric method

Ethanol zur Verwendung als Blendkomponente in Ottokraftstoff - Bestimmung des Phosphorgehaltes - Spektrometrisches Verfahren mit Ammoniummolybdat

Éthanol comme base de mélange à l'essence - Détermination de la teneur en phosphore - Méthode spectrométrique au molybdate d'ammonium

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71.080.60	Alkoholi. Etri	Alcohols. Ethers
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English Version

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN Management Centre has the same status as the official versions.

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COMITÉ EUROPÉEN DE NORMALISATION
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Contents

Page

Foreword

This document (EN 15487:2007) 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of an identical text or by endorsement, at the latest by February 2008, and conflicting national standards shall be withdrawn at the latest by February 2008.

The method described in this document is based on EN ISO 6878 [1] and a method from a European Regulation on wine [2].

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 United Kingdom.

1 Scope

This standard specifies a procedure for the determination of phosphorus content measured as orthophosphate, in ethanol from 0,15 mg/l to 1,50 mg/l by ammonium molybdate spectrometric method. The phosphorus content is determined in aqueous solution after dissolution of the evaporation residue of the ethanol sample.

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 to 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 Principle

After evaporation of the ethanol sample, the dry residue is dissolved in water. The aqueous solution is treated with an acid solution containing molybdate and antimony ions to obtain an antimony phosphomolybdate complex. The complex is then treated with ascorbic acid to form a strongly coloured molybdenum blue complex. The content of phosphorus is obtained by measuring the absorbance of the complex at 880 nm.

4 Reagents and materials

4.1 All reagents shall be of analytical reagent grade or of higher purity.

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

4.3 Sulphuric acid solution, $c(H_2SO_4) \approx 9$ mol/l
Add 500 ml ± 5 ml water (4.2) to a 2 l beaker.
Cautiously add, with continuous stirring and cooling, 500 ml ± 5 ml sulphuric acid, ρ = 1,84 g/ml.
Mix well and allow the solution to cool to room temperature.

4.4 Hydrochloric acid solution, c(HCl) ≈ 2,4 mol/l
Cautiously add in a 1 000 ml volumetric flask (5.4), 200 ml ± 10 ml of concentrated hydrochloric acid (ρ = 1,18 g/ml) to 500 ml ± 10 ml water (4.2).
Mix and cool to room temperature. Make up to 1 000 ml with water (4.2).

4.5 Sodium hydroxide solution, c(NaOH) = 2 mol/l
Dissolve 80 g ± 1 g sodium hydroxide pellets in water (4.2) in a 1 000 ml volumetric flask (5.4), cool and dilute to 1 l with water (4.2).

4.6 Ascorbic acid solution, $c(C_6H_8O_6)$ = 100 g/l
Dissolve 10 g ± 0,5 g ascorbic acid in 100 ml ± 5 ml water (4.2).

NOTE The solution is stable for 2 weeks if stored in an amber glass bottle in a refrigerator and can be used as long as it remains colourless.

4.7 Acid molybdate solution

Dissolve 13 g ± 0,5 g ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in 100 ml ± 5 ml water (4.2).
Dissolve 0,35 g ± 0,05 g antimony potassium tartrate hemihydrate [$K(SbO)C_4H_4O_6\cdot ½H_2O$] in 100 ml ± 5 ml water (4.2).
Add the molybdate solution to 300 ml ± 5 ml sulphuric acid (4.3) with continuous stirring.
Add the tartrate solution and mix well.

NOTE The reagent is stable for at least 2 months if stored in an amber glass bottle.

4.8 Orthophosphate stock standard solution, *c*(P) = 50 mg/l

Dry a few grams of potassium dihydrogen phosphate (KH_2PO_4) to constant mass at 105 °C.
Weigh about 0,220 g of KH_2PO_4 with a precision of 0,000 1 g and dissolve in about 800 ml ± 10 ml water (4.2) in a 1 000 ml volumetric flask.
Add 10 ml ± 0,5 ml sulphuric acid (4.3) and make up to the mark with water (4.2).
Alternatively, use a commercially available stock solution.

NOTE The solution is stable for at least 3 months if stored in a well stopped glass bottle. Refrigeration to about 4 °C is recommended.

4.9 Orthophosphate standard solution, *c*(P) = 2 mg/l

Pipette 20 ml ± 0,01 ml orthophosphate stock standard solution (4.8) into a 500 ml volumetric flask.
Make up to the mark with water (4.2) and mix well.
Prepare and use this solution each day as required.

5 Apparatus

5.1 Water bath

5.2 Evaporating dish, capacity 100 ml to 250 ml.

5.3 Volumetric pipettes , Class A.

5.4 Volumetric flasks, Class A.

5.5 Burettes, calibrated burettes of 10 ml and 50 ml capacity with 0,05 ml and 0,1 ml subdivision respectively.

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

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

5.8 Spectrometer, suitable for measuring absorbance at 880 nm and capable of accepting optical cells with a thickness 10 mm.

5.9 Laboratory glassware

Before use, wash all glassware, for example with hydrochloric acid (4.4), at approximately 40 °C to 50 °C and rinse thoroughly with water (4.2). Detergents containing phosphate shall not be used.

Preferably the glassware should be used only for the determination of phosphorus. After use, clean it as described above and keep covered until needed again.

Rinse glassware used for the colour development and optical cells occasionally with sodium hydroxide solution (4.5), followed by thorough rinsing with water (4.2), to remove deposits of the coloured complex which has a tendency to stick as a thin film on the wall of glassware.

6 Samples and sampling

Unless otherwise specified, laboratory samples shall be obtained by the procedures described in EN ISO 3170. High density polyethylene containers shall be used. The containers should be carefully cleaned and rinsed with pure water to avoid contamination. Particular attention should be paid to avoid contamination from phosphorus containing detergents.

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

Thoroughly mix samples in their containers immediately prior to withdrawal of the test portions.

NOTE High density polyethylene containers are used in order to prevent losses of phosphorus by wall absorption.

7 Calibration

7.1 Preparation of calibration solutions

Transfer, by means of a volumetric pipette (5.3), 2,5 ml, 5,0 ml, 10,0 ml, 20,0 ml, 30,0 ml, and 40,0 ml of orthophosphate standard solution (4.9) to 50 ml volumetric flasks. Dilute with water (4.2) to about 40 ml. As an alternative, volumes from 2,5 ml to 10,0 ml can be transferred using a 10 ml burette (5.5) and volumes from 20,0 ml to 40,0 ml using a 50 ml burette (5.5).

Transfer about 40 ml of water (4.2) to a 50 ml volumetric flask (blank solution).

7.2 Colour development

Add to each flask, while swirling, 1 ml of ascorbic acid (4.6) followed by 2 ml of acid molybdate solution (4.7). Make up to the mark with water (4.2) and mix well. Phosphorus concentration in the calibration solutions is given in Table 1.

Table 1 – Phosphorus concentration of calibration solutions

Calibration solution	Orthophosphate solution *ml*	Phosphorus concentration *mg/l*
1 (blank)	0	0
2	2,5	0,1
3	5,0	0,2
4	10,0	0,4
5	20,0	0,8
6	30,0	1,2
7	40,0	1,6

7.3 Spectrometric measurement

Set up the spectrometer (5.8) according to the manufacturer instructions.

Measure, using 10 mm cells, the absorbance of each solution at 880 nm after a period between 10 min and 30 min. Use water (4.2) in the reference cell.

7.4 Calibration regression line

Plot the absorbance (as the y-axis) against phosphorus concentration in mg/l (as the x-axis) of the calibration solutions. The relationship between absorbance and concentration is linear. Calculate the linear regression

$$Y = a \cdot X + b \quad (1)$$

where

Y is the absorbance;

X is the phosphorus concentration in mg/l;

a is the slope of the linear regression;

b is the intercept of the linear regression.

Verify the linear regression from time to time for slope and intercept, especially if new batches of chemicals are used.

8 Procedure

8.1 Dry residue

Add (50 ± 0,5) ml ethanol sample to the evaporating dish (5.2) using a 25 ml pipette (5.3). Place the dish with sample on the water bath (5.1) and allow to dry. Place the dish in the oven (5.7) at 105 °C for 30 minutes and then transfer the dish in a desiccator (5.6). Allow the dish to cool for 30 minutes.

NOTE The time usually required to obtain the dry residue ranges from 2 hours to 3 hours.

8.2 Test portion

Add about 10 ml water (4.2) to the evaporating dish (5.2) and warm gently to solubilize the dry residue. Transfer the solution to a 50 ml volumetric flask (5.4). Repeat the treatment with 10 ml water (4.2) to rinse carefully the evaporating dish (5.2) and to transfer quantitatively the residue.

8.3 Colour development

Add to the flask, while swirling, 1 ml of ascorbic acid (4.6) followed by 2 ml acid molybdate solution (4.7). Make up to the mark with water (4.2) and mix well.

8.3 Spectrometric measurement

Follow the procedure outlined in 7.3.

9 Calculation

Calculate the phosphorus content *P*, expressed in mg/l, using the equation:

$$P = \frac{A - b}{a} \quad (2)$$

where

A is the absorbance of the test portion;

b is the intercept of the calibration regression (see 7.4);

a is the slope of the calibration regression, expressed in l/mg (see 7.4).

10 Expression of results

Report the phosphorus content in mg/l, rounded to the nearest 0,01 mg/l.