SLOVENSKI STANDARD
SIST EN 15779:2009

01-december-2009

Naftni proizvodi ter maġļ obni in oljni derivati - Metilni estri maġļ obnih kislin (FAME) za dizelske motorje - Doloļ evanje polinenasiļ enih (Ó4 dvojne vezi) metilnih estrov maġļ obnih kislin (PUFA) s plinsko kromatografijo

Petroleum products and fat and oil derivates - Fatty acid methyl esters (FAME) for diesel engines - Determination of polyunsaturated (Ó4 double bonds) fatty acid methyl esters (PUFA) by gas chromatography

Mineralº lerzeugnisse und Erzeugnisse aus pflanzlichen und tierischen Fetten und ¥len - Fettsª uremethylester (FAME) f¿r Dieselmotoren - Bestimmung von mehrfach ungesª ttigten (Ó4 Doppelbindungen) Fettsª uremethylestern (PUFA) mittels Gaschromatografie

Produits p®troliers et produits d®riv®s des corps gras - Esters m®thyliques d'acides gras (EMAG) pour moteurs diesel (gazole) - D®termination de la teneur en esters m®thyliques d'acides gras polyinsatur®s (Ó4 doubles liaisons) (PUFA) par chromatographie en phase gazeuse

Ta slovenski standard je istoveten z: **EN 15779:2009**

ICS:

75.160.20	Tekoļ a goriva	Liquid fuels

SIST EN 15779:2009 **en,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15779

October 2009

ICS 75.160.20

English Version

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COMITÉ EUROPÉEN DE NORMALISATION
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Foreword

This document (EN 15779:2009) 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of an identical text or by endorsement, at the latest by April 2010, and conflicting national standards shall be withdrawn at the latest by April 2010.

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Introduction

Polyunsaturated fatty acid methyl esters are considered as a critical component in FAME since they show a low stability against oxidation and polymerization reactions. The specification on polyunsaturated ester content is needed in FAME and biodiesel products to limit the content of polyunsaturated FAME with more than three double bonds. At the time of the first FAME fuel specifications no test method was available for such a complicated determination in terms of identification and quantification, so technical work has been done in a joint working group with CEN/TC 307 before any standardisation steps could be taken.

The method has been prepared by the partners of the project "BIOScopes" (Lot 1, Task a) funded by the European Commission, DG TREN, with the purpose to execute a Pan-European round robin test to determine the precision data and the usability of this new and other revised determination methods for FAME.

1 Scope

This European Standard specifies a method for the determination of the polyunsaturated (≥ 4 double bonds) fatty acid (PUFA) methyl esters content of fatty acid methyl ester (FAME) as a whole between 0,6 % (*m/m*) and 1,5 % (*m/m*).

The method covers the predominant four polyunsaturated fatty acid methyl esters of eicosatetraenoic acid (C 20:4 (n-6)), eicosapentaenoic acid (C 20:5 (n-3)), docosapentaenoic acid (C 22:5 (n-3), and docosahexaenoic acid (C 22:6 (n-3)).

Studies have indicated that based on the linearity of results from this European Standard, PUFA methyl esters can be determined in FAME in the range between 0,3 % (*m/m*) to 3,0 % (*m/m*). However, the precision was not established in that range, as no samples within the upper ranges where included in the final interlaboratory test (see 10.1).

Although the method is applicable to all uses, it is predominantly for FAME for use in diesel engines.

NOTE 1 For the purposes of this document, the term "% (*m/m*)" is used to represent the mass fraction of a material.

NOTE 2 This European Standard is based on A.O.C.S Official Method Ce 1b-89 [1].

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 3171, *Petroleum liquids — Automatic pipeline sampling (ISO 3171:1988)*

3 Principle

Determination of the percentage of polyunsaturated (≥ 4 double bonds) fatty acid (PUFA) methyl ester present in FAME is done by gas chromatography/FID detection using internal calibration with C 23:0 methyl ester. The theoretical detector correction factors relative to C 23:0 internal standard for different poly-unsaturated ester types are applied to the analytical data for optimum accuracy.

4 Apparatus

4.1 Capable gas chromatograph, consisting of a capillary injection system (preferable split mode at a split ratio of 1:50), a flame ionization FID detector and the following:

4.1.1 Injector, temperature 220 °C.

4.1.2 Detector, temperature 275 °C.

4.1.3 Oven temperature profile, initial temperature 150 °C, initial hold time 1 min; program rate 15 °C/min up to 200 °C; 2 °C/min up to 250 °C final temperature.

4.1.4 Capillary column, fused silica; 30 m in length, 0,25 µm film thickness and 0,20 mm to 0,32 mm internal diameter. The liquid phase shall be bonded Carbowax or an equivalent polyethylene glycol type.

NOTE HP–INNOWax, SUPELCOWAX 10, Carbowax, CP-WAX 52CB and DBwax have been found satisfactory.

4.1.5 Carrier gas, hydrogen or helium of 99,99 % purity or better.

4.1.6 Additional gas, depending on instrumentation (compressed air, oxygen), but of high purity. An oxygen scrubber is mandatory with Wax-type columns.

4.1.7 Data analysis, according to the corresponding instrumentation software.

4.2 Screw-cap vials, of 1,5 ml content, with leak-tight (Teflon) lined caps.

4.3 Volumetric pipette or syringe, of 1 ml content.

4.4 Pasteur type pipettes.

4.5 Volumetric flask, of 25 ml content.

4.6 Analytical balance, capable to weigh at ± 0,1 mg.

5 Reagents and materials

5.1 Tricosanoic acid methyl ester (C 23:0), minimum purity of 99,5 %, internal standard (IS) solution, to be stored at + 4 °C and to be warmed up to room temperature before use.

NOTE If the storage conditions are maintained carefully, the solution has been found to be stable up to one month without any degradation losses.

5.2 Heptane, analytical grade.

5.3 Reference PUFA methyl esters, C 20:4 (n-6) (eicosatetraenoic acid), C 20:5 (n-3) (eicosapentaenoic acid), C 22:5 (n-3) (docosapentaenoic acid, and C 22:6 (n-3) (docosahexaenoic acid), with a minimum purity of 99,5 %.

6 Sampling

Unless otherwise specified in the commodity specification, samples shall be taken as described in EN ISO 3170 or EN ISO 3171 and/or in accordance with the requirements of national standards or regulations for the sampling of the product under test.

If it is necessary to determine PUFA methyl esters directly out of marine oils, the sample preparation should be in accordance with EN ISO 5509 [2].

7 Procedure

7.1 Weigh approx. 25 mg to the nearest 0,1 mg of internal standard (5.1) into a 25 ml volumetric flask (4.5) and fill up to mark with heptane (5.2).

7.2 Weigh approx. 100 mg to the nearest 0,1 mg of FAME into a 1,5 ml vial (4.2).

7.3 Pipette 1 ml aliquot of the Internal Standard (5.1) into the vial, cap and mix thoroughly.

7.4 Inject 1 µl of solution under appropriate gas chromatographic conditions (see 4.1).

8 Calculation

The PUFA content, C, expressed in mass percentage, is calculated according:

$$C = \frac{\sum (A_{PUFA} \times CF_{PUFA})}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m} \times 100 \quad (1)$$

where:

A_{IS} is the peak area of the internal standard C 23:0;

A_{PUFA} are the peak areas of the polyunsaturated fatty acid methyl esters (see Figure 1);

C_{IS} is the concentration in mg/ml of the internal standard;

CF_{PUFA} are the theoretical correction factors of the corresponding PUFA methyl esters (see below);

V_{IS} is the volume in ml of the internal standard added;

m is the mass in mg of the sample (see 7.2).

Identification of the polyunsaturated fatty acid methyl esters has to be done by using the reference PUFA methyl esters (5.3).

The following theoretical detector correction factors (CF_{PUFA}) relative to C 23:0 shall be applied to the calculation for optimum accuracy (see also Figure 1):

a) 20:4 n-6: 0,99;

b) 20:5 n-3: 0,98;

c) 22:5 n-3: 0,98; and

d) 22:6 n-3: 0,97.