BRITISH STANDARD

BS EN
14110:2003

Fat and oil derivatives — Fatty Acid Methyl Esters (FAME) — Determination of methanol content

The European Standard EN 14110:2003 has the status of a British Standard

ICS 67.200.10

National foreword

This British Standard is the official English language version of EN 14110:2003.

The UK participation in its preparation was entrusted to Technical Committee AW/307, Oilseed animal & vegetable fats and oils, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled "International Standards Correspondence Index", or by using the "Search" facility of the *BSI Electronic Catalogue* or of British Standards Online.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 15 May 2003

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 10, an inside back cover and a back cover.

The BSI copyright notice displayed in this document indicates when the document was last issued.

Amendments issued since publication

Amd. No.	Date	Comments

ISBN 0 580 41842 1

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 14110

April 2003

ICS 67.200.10

English version

Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) - Determination of methanol content

Produits dérivés des corps gras - Esters méthyliques d'acides gras (EMAG) - Détermination de la teneur en méthanol

Erzeugnisse aus pflanzlichen und tierischen Fetten und Ölen - Fettsäure-Methylester (FAME) - Bestimmung des Methanolgehaltes

This European Standard was approved by CEN on 2 January 2003.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

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 Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and United Kingdom.

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

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 14110:2003 E

Foreword

This document (EN 14110:2003) has been prepared by Technical Committee CEN/TC 307 "Oilseeds, vegetable and animal fats and oils and their by-products - Methods of sampling and analysis", the secretariat of which is held by AFNOR.

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 2003, and conflicting national standards shall be withdrawn at the latest by October 2003.

This document has been prepared under Mandate M/245 on Fatty Acid Methylester (FAME) given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

Annexes A and B are informative.

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

1 Scope

This European Standard specifies a method for the determination of methanol content in fatty acid methyl esters (FAME) for use as diesel fuel and domestic heating fuel. The method is applicable for a concentration range from 0,01 % (*m/m*) to 0,5 % (*m/m*) methanol. The method is not applicable to mixtures of FAME which contain other low boiling components.

2 Principle

The sample is heated at 80 °C in a hermetically sealed vial to allow desorption of contained methanol into the gas phase. When equilibrium is reached, a defined part of the gas phase is injected into a gas chromatograph, where methanol is detected with a flame ionisation detector. Normally methanol is the only peak in the chromatogram.

The amount of methanol is calculated by reference to an external calibration. Methanol can also be determined after addition of an internal standard to the sample before heating, followed by calculation with the use of an internal calibration factor.

NOTE If only manual equipment is available then only internal standard calibration should be used.

3 Reagents

Use only reagents of recognized analytical grade, unless otherwise specified.

3.1 Methanol, of known purity greater than 99,5 %.

3.2 2-propanol, of known purity, greater than 99,5 % (for procedure A, internal calibration).

3.3 Reference FAME, with a methanol content less than 0,001 % (*m/m*).

NOTE Reference FAME can either be obtained from commercial sources or by washing by three or five times with distilled water in a separator funnel. FAME should be then dried by heating at 90 °C under stirring and reduced pressure.

3.4 Carrier gas, nitrogen, helium or hydrogen, of know purity greater than 99 %.

4 Apparatus

4.1 Septum vials, 20 ml capacity.

4.2 Inert septa (e.g. TFE or Viton [1)]) **and metallic caps**.

4.3 Syringe, 10 µl, accurate to 0,1 µl.

4.4 Gas syringe 500 µl, fitted with a valve (for manual procedure).

4.5 Crimping pliers.

4.6 Pipettes, of 1 ml, 2 ml, 5 ml capacity.

4.7 Volumetric flask, capacity 10 ml and 25 ml.

1) This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of these products. Equivalent products may be used if they can be shown to lead to the same results.

4.8 Gas chromatograph, equipped with a capillary column, suitable injector (automatic headspace system or a split/splitless injector) and flame ionisation detector, integrator.

4.9 Capillary column, the column shall eluate methanol as a symmetrical peak. Stationary phases like methylpolysiloxane (e.g. DB1 [2)], SE30 [2)]) or polyethylenglycol (e.g. DBWAX [2)], CAR-BOWAX [2)]) can be used successfully and a film thickness of minimum 0,5 µm is recommended.

NOTE The use of a packed column equipped by one of the above mentioned stationary phases or of Chromosorb 101[2)] is also allowed.

4.10 Automatic headspace equipment

The automatic headspace equipment used shall have a repeatability of 1 % or better concerning experimental conditions like equilibrium temperature, heating times, and headspace sampling volume. This can be checked, if necessary, by repeated analysis of the same sample.

NOTE Automatic headspace equipment is recommended because apart, from its better repeatability, it allows for automated and fast analysis using external calibration. Manual equipment can also be used, however, extreme care should be exercised when gas volumes are taken manually from the vials and when injecting them into the gas chromatograph.

4.11 Analytical balance with a resolution of 0,0001 g.

4.12 Thermostatically controlled bath or oven, 80 °C.

4.13 Thermostatically controlled oven, 60 °C.

5 Procedure

5.1 Analytical conditions

The GC working conditions shall be chosen taking into account the characteristics of the column and the type of carrier gas to reach the desired resolution which is fixed at minimum 1,5 for the methanol and 2-propanol peaks.

NOTE 1 The following parameters are given as an example:

— column DB1 (length = 30 m, internal diameter = 0,32 mm, film thickness = 3 µm);

— split injector (flow rate : 50 ml/min);

— injector and detector temperature : 150°C;

— oven and column temperature : 50 °C;

— carrier gas (hydrogen) pressure : 40 kPa;

— volume injected : 500 µl.

NOTE 2 The following head space sampling conditions are given as an example:

— equilibrium temperature : 80 °C;

— equilibrium time : 45 min;

— sampling volume : 500 µl.

2) This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of these products. Equivalent products may be used if they can be shown to lead to the same results.

5.2 Operation

The gas chromatograph shall be set up and operated according to the manufacturer's instructions.

6 Calibration solutions

Three calibration solutions with approximately the following methanol concentrations in FAME (3.3) shall be prepared as described below.

NOTE Three calibration solutions have proven sufficient in daily practise for a reliable coverage of the concentration range given in the scope of this method. For other concentration ranges, it is also possible to use other or more calibration solutions.

6.1 Calibration solution A (0,5 % (*m/m*) methanol in FAME).

Fill a 25 ml volumetric flask with 25 ml of FAME (3.3) and add (112 ± 0,1) mg (142 µl) methanol into the liquid phase using a syringe (4.3), the addition being made into the liquid phase. The exact masses shall be determined by weight measurement. It is necessary to ensure thorough mixing by vigorous shaking.

6.2 Calibration solution B (0,1 % (*m/m*) methanol in FAME).

Transfer 5 ml of calibration solution A into a 25 ml analytical flask and carefully fill to the mark with FAME (3.3).

6.3 Calibration solution C (0,01 % (*m/m*) methanol in FAME).

Transfer 1 ml of calibration solution B into a 10 ml analytical flask and fill to the mark with FAME (3.3).

7 Procedure

Two alternative procedures, the first using internal calibration and the second using external calibration are described in clauses 7.1 and 7.2, respectively.

7.1 Procedure A - Using internal calibration

This procedure is generally preferred when only a small number of samples is analyzed and when automatic head space equipment is not available. For manual procedure, see note in clause (4.10).

7.1.1 Internal calibration

(5 ± 0,01) g from each calibration solution is transferred into a head space vial (4.1) and 5 µl of 2-propanol (3.2) is added into the liquid phase using a syringe (4.3), the addition being made into the liquid phase. The vials are then immediately crimped and shaken vigorously to ensure mixing.

Every 10 min, introduce into thermostatically-controlled bath or oven (4.12) a vial of the calibration solution which shall be kept there for exactly 45 min.

Preheat the gas syringe (4.4) to 60 °C in an oven (4.13). Sample 500 µl of gaseous phase (headspace) above the solution to be analysed and carry out the chromatographic analysis.

The calibration factor F is calculated for each calibration solution according to equation (1), shall be expressed rounded to the nearest 0,01.

$$F = \frac{(C_m \times S_i)}{(C_i \times S_m)} \qquad (1)$$

where

C_{i} is the 2-propanol content in the calibration solution, expressed in % (*m/m*);

(If 5 µl of 2-propanol are introduced into 5,0 g calibration solution, then C_i = 0,0785 % (*m/m*)).

C_m is the methanol content in the calibration solution, expressed in %(*m/m*);

S_i is the peak area of 2-propanol;

S_m is the peak area of methanol.

The calibration factor values obtained for the three reference solutions shall exhibit a coefficient of variation below 15 %. If this value is exceeded, the experimental set-up shall be inspected for errors and the calibration procedure shall be repeated starting from clause (6). The mean of these calibration factor values (in the region of 0,7) is used for the calculation described in clause 7.1.2.

7.1.2 Analysis and Calculation using internal calibration

The samples shall be prepared and analysed with exactly the same experimental conditions used in the calibration runs (7.1.1). The methanol content C_m of a sample, expressed in % (*m/m*), is calculated according to equation (2) and rounded to two decimal places:

$$C_m = \frac{F \times S_m \times C_i}{S_i} \quad (2)$$

where

F is the calibration factor obtained according to clause 7.1.1;

S_m is the peak area of methanol;

C_i is 2-propanol content added to the sample, expressed in % (*m/m*);

(If 5 µl of 2-propanol are introduced into 5,0 g sample, then C_i = 0,0785 %(*m/m*)).

S_i is the peak area of 2-propanol.

7.2 Procedure B - Using external calibration

This procedure is usually preferred when automatic head space equipment is used and a large number of sampled is analysed. It is not recommended to use external calibration when the analysis is executed manually, i.e. without automatic head space equipment.

7.2.1 External calibration

2 ml from each calibration solution is transferred into a head space vial. The vial shall be crimped immediately. The vials are then placed into the head space sampler and the analysis is started according to the manufacturer's instruction manual.

The calibration function is calculated using linear regression, using the methanol contents as dependent variable and the peak areas as independent variable. Using the resulting slope, d, and y-intercept, e, the regression function is then converted using equation (3):

$$C_m = a + b \times S_m \quad (3)$$

where

C_m is the methanol content in % (*m/m*);

a is the coefficient obtained from (- e/d);

b is the coefficient obtained from (1/d);

S_m is the area of the methanol peak;

d is the slope of regression line;

e is y intercept of regression line.

NOTE If the correlation coefficient is less than 0,95, the procedure should be inspected for errors and the calibration procedure should be repeated starting with clause 6.

7.2.2 Analysis and calculation using external calibration

The samples shall be prepared and analysed with exactly the same experimental conditions used in the calibration runs (7.2.1). The methanol content C_m of a sample, expressed in % (m/m), is calculated according to equation (3) and rounded to the nearest 0,01 % (m/m).

8 Precision

The precision data for procedure A and procedure B have both been obtained from a European interlaboratory trial organised in 1999. In this round robin exercise, no significant differences were observed between procedure A and procedure B (with automatic headspace system or with manual procedure) for the methanol concentration range of 0,01 % to 0,20 % (m/m).

8.1 Repeatability

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short time interval, shall not be greater than:

$$r = 0{,}056 \cdot X + 0{,}001 \quad (4)$$

more than once out of 20 determinations (X being the mean of the two results in question).

8.2 Reproducibility

The absolute difference between two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, shall not be greater than:

$$R = 0{,}221 \cdot X + 0{,}003 \quad (5)$$

more than once out of 20 determinations (X being the mean of the two results in question).

9 Test report

The test report shall specify:

— all information necessary for the complete identification of the sample;

— the sampling method used if known;

— the test method used, with reference to this European standard;

— all operating details not specified in this European Standard, or regarded as optional, together with details of any incidents which may have influenced the test result(s);

— the test result(s) obtained, or if the repeatability has been checked, the final quoted result obtained.

Annex A
(informative)

Results of an interlaboratory trial

A European collaborative test involving 10 laboratories in 6 countries was carried out on 5 samples:

Sample 1 : FAME prepared from a mixture of rapeseed and sunflower oils (25:75);

Sample 2 : FAME prepared from sunflower oil;

Sample 3 : FAME prepared from rapeseed oil;

Sample 4 : FAME prepared from a mixture of rapeseed and sunflowers oils (75:25);

Sample 5 : FAME prepared from rapeseed oil.

The test was organized by CEN TC 307/WG1 in 1999 and the results obtained were subjected to statistical analysis in accordance with EN ISO 4259 [1] to give the precision data shown in Tables A.1 to A.2.

Table A.1 — Internal calibration

Sample	1	2	3	4	5
N° of participating laboratories	10	10	10	10	10
N° of participating laboratories after eliminating outliers	8	8	9	9	8
Mean value (% *m/m*)	**0,071**	**0,105**	**0,008**	**0,020**	**0,136**
Repeatability standard deviation (% *m/m*)	0,002	0,003	0,000	0,001	0,030
Reproducibility standard deviation (% *m/m*)	0,007	0,013	0,001	0,003	0,011
Repeatability limit, r (% *m/m*)	0,005	0,008	0,001	0,002	0,008
Reproducibility limit, R (% *m/m*)	0,018	0,037	0,003	0,007	0,030

Table A.2 — External calibration

Sample	1	2	3	4	5
N° of participating laboratories	8	8	8	8	8
N° of participating laboratories after eliminating outliers	6	7	7	7	7
Mean value (% *m/m*)	**0,063**	**0,097**	**0,007**	**0,017**	**0,122**
Repeatability standard deviation (% *m/m*)	0,001	0,003	0,001	0,001	0,002
Reproducibility standard deviation (% *m/m*)	0,006	0,009	0,002	0,003	0,010
Repeatability limit, r (% *m/m*)	0,004	0,008	0,002	0,002	0,006
Reproducibility limit, R (% *m/m*)	0,016	0,025	0,004	0,008	0,027

Annex B
(informative)

Figure B.1

Key

1 Methanol (0,12 %)
2 2-propanol (0,08 %)

Figure B.1 — Chromatogram of rapeseed FAME sample — Determination of methanol content (the analytical conditions are given in 5.1)

Bibliography

[1] EN ISO 4259, *Petroleum products - Determination and application of precision data in relation to methods of test (ISO 4259:1992/Cor 1:1993).*

blank

BSI — British Standards Institution

BSI is the independent national body responsible for preparing British Standards. It presents the UK view on standards in Europe and at the international level. It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover. Tel: +44 (0)20 8996 9000. Fax: +44 (0)20 8996 7400.

BSI offers members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Buying standards

Orders for all BSI, international and foreign standards publications should be addressed to Customer Services. Tel: +44 (0)20 8996 9001. Fax: +44 (0)20 8996 7001. Email: orders@bsi-global.com. Standards are also available from the BSI website at http://www.bsi-global.com.

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Library and its Technical Help to Exporters Service. Various BSI electronic information services are also available which give details on all its products and services. Contact the Information Centre. Tel: +44 (0)20 8996 7111. Fax: +44 (0)20 8996 7048. Email: info@bsi-global.com.

Subscribing members of BSI are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration. Tel: +44 (0)20 8996 7002. Fax: +44 (0)20 8996 7001. Email: membership@bsi-global.com.

Information regarding online access to British Standards via British Standards Online can be found at http://www.bsi-global.com/bsonline.

Further information about BSI is available on the BSI website at http://www.bsi-global.com.

Copyright

BSI
389 Chiswick High Road
London
W4 4AL