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Fatty acid methyl esters (FAME) — Determination of sulfur content — Inductively coupled plasma optical emission spectrometry (ICP-OES) method

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National foreword

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Fatty acid methyl esters (FAME) — Determination of sulfur content — Inductively coupled plasma optical emission spectrometry (ICP-OES) method

Esters méthyliques d'acides gras — Détermination de la teneur en soufre — Méthode par spectroscopie d'émission optique par plasma à couplage inductif (ICP-OES)

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This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*, Subcommittee SC 7, *Liquid Biofuels*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document seeks to evaluate the quality of fatty acid methyl esters (FAME) in terms of sulfur.

Though FAME itself does not contain sulfur, sulfur might occur as contaminant either in feedstock, due to the use of fertilizers, or in production processes using sulfuric acid. The presence of sulfur in FAME can be caused by the production process of FAME and/or possible contaminations by diesel fuel. Above certain levels of sulfur concentration, it can be harmful to use FAME as fuel. The test method provided in this document offers a simple and effective way to check and control the sulfur level of FAME, which is used as pure fuel or as blend component.

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INTERNATIONAL STANDARD ISO 20424:2019

Fatty acid methyl esters (FAME) — Determination of sulfur content — Inductively coupled plasma optical emission spectrometry (ICP-OES) method

WARNING — The use of this document can involve hazardous materials, operations and equipment. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel prior to the application of this document, and to determine the applicability of any other restrictions.

1 Scope

This document specifies a test method for inductively coupled plasma optical emission spectrometry (ICP-OES) for the detection of the sulfur content from 2 mg/kg to 21 mg/kg in fatty acid methyl esters (FAME).

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

NOTE 2 The method can also be used for the determination of concentrations outside the given limits. The precision statement, however, is only valid for the concentration range given in the scope.

NOTE 3 The method described in the document was tested with FAME derived from soybean oil and beef tallow. FAME derived from other feedstock, in particular aged oils, may behave different due to the different nature of sulfur compounds.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 3170, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

An exactly weighed test portion is diluted with kerosene to allow the proper introduction of the aerosol into the plasma. The resulting solution is directly injected into the plasma of the ICP-OES spectrometer.

7 Sampling

Samples shall be taken as described in ISO 3170 or ISO 3171.

8 Preparation of stock solution and calibration solution

8.1 Stock solution

Sulfur solution with a concentration of 50 mg/kg: add to an appropriate conical flask (6.4) approximately 3,0 g of the standard sulfur solution (5.3), fill up to 30 g with diluent (5.1).

Weigh the masses with an accuracy of 0,000 1 g and homogenize the solution. Calculate the exact concentration of this solution, which shall be used to prepare the calibration solutions.

It is also permitted to prepare the dilution on volumetric basis. In this case, use appropriate pipettes (6.5) to transfer the volumes. In this case the concentration is expressed as mass/volume.

Other concentrations and quantities can be used for the stock solution but the precision data in Clause 10 were obtained from analysis with the given concentration above.

8.2 Preparation of the calibration solutions

The calibration solutions are prepared from an organic sulfur compound which is commercially available. The sulfur compound is diluted in a mixture of diluent (6.1) and base oil (6.2). The addition of the base oil has the objective to reduce the differences in viscosity between the samples and the calibration solutions.

8.2.1 Blank solution for sulfur

Prepare an adequate amount of a solution of 10 % (*m/m)* low viscosity oil (5.2) in the solvent (5.1).

WARNING — When using other oils (see Note to 5.2) the concentration of low viscosity oil in the blank solution shall be calculated as described in Annex A.

8.2.2 Calibration sample set

Table 1 shows the recommended calibration set for sulfur (0,0 mg/kg, 1,0 mg/kg, 2,5 mg/kg, 5,0 mg/kg and 10 mg/kg).

Weigh the masses with an accuracy of 0,000 1 g into the flask and fill up to the given amount with blank solution (8.2.1). Stir the samples until the homogenization is complete.

Calculate the exact concentrations of the calibration solutions for given in Table 1.

When the concentrations of the solutions are expressed in mass/volume percentages (8.1), the calibration solutions shall be expressed in the same way.

For each calibration, freshly prepared calibration samples shall be used.

Table 1 — Calibration solutions

Sulfur content mg/kg	Stock solution g	Total quantity g
0	0	10
1,0	0,2	10
2,5	0,5	10
5,0	1,0	10

Sulfur content mg/kg	Stock solution g	Total quantity g
10,0	2,0	10

NOTE Depending on the instrument larger calibration samples might be necessary in order to have suitable amounts for repeat measurement.

9 Calibration

Run the measurements of the calibration solutions, with at least three readings of each one.

Calculate the arithmetic average of the three measurements, for each solution. From these averages, associate the intensity values to the respective concentration values for the calibration solutions, expressed in milligrams per kilogram, using a linear regression to obtain the calibration curve.

In the case of using a mass/volume relationship, express the concentration values for the calibration solutions in mg/l.

NOTE In the ILS, each calibration sample was measured three times.

10 Procedure

10.1 Sample preparation

The FAME sample shall be clear and bright. In case of a turbid sample, heat to a temperature of 50 °C for 10 min. If after heating and homogenization the sample is still turbid, this sample shall be discarded.

NOTE This procedure is based on ISO 661[1]. The drying procedure described in that document cannot be executed.

The sample shall be prepared adding 5,0 g of sample, with a resolution of 0,000 1 g, in adequate flasks. Complete to 25 g with the same solvent used in 8.1 and stir until completely homogenized. This procedure shall be executed at least in duplicate.

10.2 Instrument optimization

Since instruments from different manufacturers have distinct configurations and settings, it is difficult to define the optimal instrument parameters in advance. The manufacturer's instructions should be followed, adjusting parameters, such as the flows of auxiliary gas, nebulization, refrigeration, radiofrequency power, sample aspiration rate, among others.

The selection of the experimental parameters shall be executed in order to obtain a better signal-to-noise ratio.

The recommended wavelengths are 180,669 nm and 181,975 nm.

For organic solutions, the operating guidelines should be followed:

a) temperature of spray chamber should be optimised, depending on sample matrix;

b) radiofrequency power generally 30 % greater than the power used for aqueous solutions;

c) aspiration rate generally lower than those used for aqueous solutions.

10.3 Sample measurement

Proceed to the measurements of the solution of the sample as per the procedure adopted in the calibration solutions.

It is recommended to verify the stability of the instrument by checking one of the calibration solutions at regular intervals during the measurement of the samples. If the results of this examination differ by more than the repeatability (13.2) from the results obtained during the calibration experiment, a new calibration curve shall be established.

The intensity of the analytical line corresponds to the value of the maximum intensity subtracted from the background intensity. The selected line shall present the best signal-to-noise ratio.

11 Expression of the results

When the concentrations of the calibration solutions are expressed as mass/mass, obtain the concentration C (in milligrams per kilogram) of sulfur in the sample using the analytical curve and multiplying by the dilution factor.

If the result has been obtained in mass/volume (milligrams per litre), use the calibration curve, multiply by the dilution factor and apply Formula (1):

$$C = \frac{c}{d} \tag{1}$$

where

C is the sulfur concentration in the sample, expressed in milligrams per kilogram (mg/kg);

c is the sulfur concentration in the reading sample, expressed in milligrams per litre (mg/l);

d is the average density of FAME, the attributed value of which is 0,88 g/ml at 20 °C.

The value attributed to the density d is not valid for predominantly lauric acid FAME samples (for example coconut or palm kernel FAME). In this case, one shall measure the density at 20 °C in accordance with ISO 12185.

The average concentration (C_m) of sulfur in the sample is the arithmetic mean of two independent measurements on the same sample. Report the result in milligram per kilogram, rounded to the next 0,1 mg/kg.

12 Quality control

Confirm the accuracy of the test using a reference sample, with a maximum tolerance of 10 % in relation to the reference value.

13 Precision

13.1 Interlaboratory study

The precision, as determined by statistical examination in accordance with the ISO 4259 series[3] on interlaboratory test, results of a matrix of fuels as given in Annex B. The values derived from these tests might not be applicable to concentration ranges and matrices other than those given.

In the interlaboratory study, only FAME produced from beef tallow and from soybean oil were used. Other FAME might cause accuracy problems due to the potentially different nature of sulfur compounds contained.

13.2 Repeatability, *r*

The difference between two independent results obtained in the normal and correct operation of the same method, for test material considered to be the same, within a short interval of time, under the

same test conditions, that is expected to be exceeded with a probability of 5 % due to random variation, can be calculated using Formula (2):

$$r = 0{,}1276(X + 3{,}5060) \tag{2}$$

where X is the average of the two test results being compared.

13.3 Reproducibility, R

The difference between two independent results obtained in the normal and correct operation of the same method, for test material considered to be the same, under different test conditions, that is expected to be exceeded with a probability of 5 % due to random variation, can be calculated using Formula (3):

$$R = 0{,}1627(X + 3{,}5060) \tag{3}$$

where X is the average of the two test results being compared.

14 Test report

The test report shall contain at least the following information:

a) a reference to this document, i.e. ISO 20424:2019;

b) the type and complete identification of the product tested;

c) the result of the test (Clause 8);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.

Annex A
(normative)

Calculation of the concentration of low viscosity oil in the blank solution

In order to obtain concentration (mass/mass) of low viscosity oil in the blank solution, the desired dilution factor for the samples shall be defined. Once this factor has been set, Formulae (A.1) and (A.2) shall be used for the calculation of the concentration:

$$C_{\text{oil}} = \frac{logv_{\text{b}} - logv_{\text{s}}}{logv_{\text{o}} - logv_{\text{s}}} \times 100 \tag{A.1}$$

where

C_{oil} is the concentration in mass/mass percentage of low viscosity oil in the blank solution;
v_{b} is the viscosity of the diluted sample;
v_{s} is the viscosity of the solvent used;
v_{o} is the viscosity of the low viscosity oil.

$$logv_{\text{b}} = \frac{1}{f} \times logv_{\text{B}} + \left(1 - \frac{1}{f}\right) \times logv_{\text{s}} \tag{A.2}$$

where

v_{B} is the viscosity of FAME;
f is the dilution factor.

It is considered that the viscosity of FAME is 4,5 mm^2/s at 40 °C. All the viscosities considered are in mm^2/s at 40 °C.

The viscosity may be obtained alternatively by ISO 3104.

Example

Considering a low viscosity oil of 33,5 mm^2/s at 40 °C, a commercial kerosene with about 1,5 mm^2/s at 40 °C of viscosity and a sample dilution factor of 5:

$$logv_{\text{b}} = \frac{1}{5} \times log4{,}5 + \left(1 - \frac{1}{5}\right) \times log1{,}5$$

$$logv_{\text{b}} = 0{,}272$$

$$C_{\text{oil}} = \frac{0{,}272 - \log 1{,}5}{log33{,}5 - log1{,}5} \times 100$$

$$C_{\text{oil}} = \frac{0{,}095\,9}{1{,}349\,0} \times 100 \cong 7{,}1\,\%$$

In this case, a blank solution with about 7 % (*m*/*m*) of low viscosity oil shall be prepared instead of 10 % (*m*/*m*).

Annex B
(informative)

Interlaboratory study — Used FAME samples to provide precision data

Table B.1 presents the FAME products used during the interlaboratory study

Table B.1 — Sample matrix

Sample	Feedstock composition	Estimated sulfur content mg/kg
1	Soybean	5
2	Soybean	10
3	Soybean	25
4	Soybean (82 %)/Beef tallow (18 %)	4
5	Soybean (82 %)/Beef tallow (18 %)	12
6	Soybean (82 %)/Beef tallow (18 %)	16
7	Soybean (60 %)/Beef tallow (40%)	4
8	Soybean (60 %)/Beef tallow (40 %)	8
9	Soybean	2,5

Bibliography

[1] ISO 661, *Animal and vegetable fats and oils — Preparation of test sample*

[2] ISO 3104, *Petroleum product — Transparent and opaque liquids — Determination of the kinematic viscosity and the calculation of the dynamic viscosity*

[3] ISO 4259 (all parts), *Petroleum and related products — Precision of measurement methods and results*

[4] ISO 20846, *Petroleum products — Determination of sulfur content of automotive fuels — Ultraviolet fluorescence method*

[5] ASTM D5453, *Determination of total sulfur in light hydrocarbons, spark ignition engine fuel, diesel engine fuel, and engine oil by ultraviolet fluorescence*

[6] ABNT NBR 15867, Biodiesel — Determinação do teor de enxofre por espectrometria de emissão atômica com plasma indutivamente acoplado (ICP-OES) — ABNT NBR 15867: 2010

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