SLOVENSKI STANDARD

SIST EN 14538:2006

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Derivati maġļ ob in olj ï Metil estri maġļ obnih kislin (FAME) ï Doloļ evanje Ca, K, Mg in Na z optiļ no emisijsko spektometrijo z induktivno sklopljeno plazmo (ICP OES)

Fat and oil derivatives - Fatty acid methyl ester (FAME) - Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES)

Erzeugnisse aus pflanzlichen und tierischen Fetten und Ölen - Fettsäure-Methylester (FAME) - Bestimmung des Ca-, K-, Mg- und Na-Gehaltes durch optische Emissionsspektralanalyse mit induktiv gekoppeltem Plasma (ICP OES)

Produits dérivés des corps gras - Esters méthyliques d'acides gras (EMAG) - Détermination de la teneur en Ca, K, Mg et Na par spectrométrie d'émission optique avec plasma a couplage inductif (ICP OES)

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This European Standard was approved by CEN on 10 May 2006.

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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 Central Secretariat has the same status as the official versions.

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COMITÉ EUROPÉEN DE NORMALISATION
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Foreword

This document (EN 14538:2006) 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of an identical text or by endorsement, at the latest by December 2006, and conflicting national standards shall be withdrawn at the latest by December 2006.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, 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 document specifies a procedure for the direct determination of the soap building elements Calcium (Ca), Magnesium (Mg), Sodium (Na) and Potassium (K) in fatty acid methyl esters (FAME) by ICP OES at levels of about 1 mg/kg to 10 mg/kg.

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

An exactly weighed test portion is diluted with kerosene using a 1:1 weight ratio. The resulting solution is directly injected into the plasma of the ICP OES spectrometer. For reference and calibration purposes, calibration samples with known contents of the element(s) under investigation in the range of 0,5 mg/kg to 10 mg/kg are used. The sum of the content of Calcium and the content of Magnesium, and the sum of the content of Sodium and the content of Potassium are reported.

4 Chemicals

Unless otherwise stated, only chemicals of recognized analytical quality shall be used.

4.1 Paraffin oil, low viscosity, Pharmacopeia (EUPHARM EP5), e.g. Merck 107174[1)]

4.2 Kerosene, boiling range included between 150 °C and 325 °C, e.g. Aldrich 32.946-0[1)]

4.3 Element Standard solutions, dissolved in oil, 500 mg/kg per element. These are available as single element standards, like e.g. Merck 115053 (Ca), 115057 (Mg), 115054 (K) and 115058 (Na), or also at least partially as multi-element standards, (e.g. Spex)[1)].

4.4 Argon, with minimum purity *w* (Ar) = 99,996 % *(V/V)*

5 Apparatus

Commercial laboratory and glass equipment, in conjunction with the following:

5.1 100 ml bottles with cap, preferably made of Polyethylene (PE), brown

5.2 250 ml bottles with cap, preferably made of Polyethylene (PE), brown

1) Merck, Aldrich and Spex standards are examples of a suitable product available commercially. This information is given for the convenience of users of this standard and does not constitute an endorsement by CEN of these products.

NOTE In order to minimize pollution of the solutions, it is recommended to prepare all the determination solutions in polyethylene bottles. Do not touch surfaces that could come in contact with working solutions. New glassware should be filled with sodium-free water and to be left for two days before use to remove soluble sodium. This is especially important when this procedure is used for the determination of sodium and/or potassium.

5.3 ICP OES spectrometer

5.3.1 General

ICP OES spectrometers (simultaneous or sequence devices) equipped for the analysis of organic liquids are suitable. Both setup and operation of the ICP OES spectrometer shall be done in accordance with operating instructions of the manufacturer.

NOTE 1 Depending on the type and construction of the ICP OES spectrometer (radial, axial, detectors sensitivity, etc.) it may sometimes be necessary to select wavelengths different from those listed here. In such cases, a separate optimization of the instrument parameters and possibly also of the optimal dilution (see 9.1) is strongly recommended.

NOTE 2 The calibration solution with an element content of 1 mg/kg (7.4) can be used to check the correct instrument performance.

5.3.2 Recommended wavelengths for Calcium and Magnesium

The following wavelengths are recommended for the analysis, because they have been found to exhibit minimal interference in daily practice:

Calcium 422,673 nm;

Magnesium 279,553 nm.

Depending on the ICP OES spectrometer's optical configuration also other specific wavelengths can be selected, like 317,933 nm, 393,366 nm or 396,847 nm for Calcium and 285,213 nm for Magnesium, if these lines are free from interferences (see also Note 1 under 5.3.1).

5.3.3 Recommended wavelengths for Sodium and Potassium

The following wavelengths are recommended for the analysis, because they have been found to exhibit minimal interference in daily practice (see also Note 1 under 5.3.1).

Sodium 588,995 nm or 589,592 nm;

Potassium 769,897 nm or 766,490 nm.

6 Sampling

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 automotive diesel fuel. Bottles made of plastic (PE or PTFE) preferably should be used.

7 Preparation of the calibration solutions and the blank solution

7.1 General

In order to avoid inhomogenities, the standard solutions (4.3) should be shaken vigorously before use.

The masses given in 7.3, 7.4, 7.5 and 7.6 correspond to a nominal element content of 500 mg/kg per element in the standard solutions (4.3) and (4.4). Calculate the exact concentrations for the calibration solutions, taking into account the exact weights. All prepared solutions shall be homogenized by vigorous shaking.

NOTE 1 As a strong general recommendation, the solutions used for calibration should be freshly prepared. If that is not possible, the samples should be stabilized using a suitably small amount of a stabilizing agent like 2-Ethylhexanoic acid, which has been shown to be free of the elements under investigation. Experience from daily practice has shown that such stabilized samples can be used for about 14 days. However, there is also sufficient evidence that calibration standard (7.3) in particular is not sufficiently stable, so that it is strongly recommended to prepare fresh solutions for each new calibration.

NOTE 2 The dilution factors for the blank solution, the calibration solutions and sample solution should be selected such that the viscosities are as close to one another as possible. This can often be achieved by using a somewhat higher dilution factor.

7.2 Blank solution

Approximately 30 g paraffin oil (4.1) is weighed, with a precision of 0,01 g, into a 250 ml PE bottle (5.2), filled up with kerosene (4.2) to a total sample mass of approximately 100 g, with a precision of 0,01 g.

7.3 Calibration solution with a nominal element content of 0,5 mg/kg

For each element, approximately 0,1 g standard solution (4.3) is weighed, with a precision of 0,000 1 g, into a 250 ml PE bottle (5.2). Then approximately 30 g paraffin oil is added, with a precision of 0,01 g. Subsequently, kerosene (4.2) is added to make up to a total sample weight of approximately 100 g, with a precision of 0,01 g.

Special attention shall be executed in using this calibration solution, as it is not as stable as the other ones.

7.4 Calibration solution with a nominal element content of 1 mg/kg

For each element, approximately 0,2 g standard solution (4.3) is weighed, with a precision of 0,000 1 g, into a 250 ml PE bottle (5.2). Then approximately 30 g paraffin oil is added, with a precision of 0,01 g. Subsequently, kerosene (4.2) is added to make up to a total sample weight of approximately 100 g, with a precision of 0,01 g.

7.5 Calibration solution with a nominal element content of 5 mg/kg

For each element, approximately 1 g standard solution (4.3) is weighed, with a precision of 0,000 1 g, into a 250 ml PE bottle (5.2). Then approximately 30 g paraffin oil is added, with a precision of 0,01 g. Subsequently, kerosene (4.2) is added to make up to a total sample weight of approximately 100 g, with a precision of 0,01 g.

7.6 Calibration solution with a nominal element content of 10 mg/kg

For each element, approximately 2 g standard solution (4.3) is weighed, with a precision of 0,000 1 g into a 250 ml PE bottle (5.2). Then approximately 30 g paraffin oil is added, with a precision of 0,01 g. Subsequently, kerosene (4.2) is added to make up to a total sample weight of approximately 100 g, with a precision of 0,01 g.

8 Calibration

8.1 General

The ICP OES spectrometer setup and instrument check is performed according to the instructions from the manufacturer. A separate calibration function for each element under investigation shall be established.

8.2 Calibration

The calibration of the ICP OES spectrometer shall be done by the measurement of the blank solution (7.2) and of the standard solutions (7.3 to 7.6). For the determination of the elements the wavelengths recommended in 5.3 shall be used. It is important to ensure that the wavelengths used in calibration also match exactly the ones used in the measurement.

For each element under investigation, a calibration curve is constructed using linear regression with concentration as independent variable (X) and signal as dependent variable (Y). This can either be done manually or with use of a computer. The calibration curve will have the form $Y = m \times X + b$, where m is the slope and b is the Y-intercept for the regression line.

8.3 Check of calibration

The calibration curves shall be checked in regular intervals. In practice, at least two points of each calibration curve have to be checked every day. If the results of this examination differ by more than the repeatability (see 12.1) from the results obtained during the calibration experiment, a new calibration curve shall be established (see also Note 1 under 7.1).

9 Sample analysis

9.1 Sample preparation

The sample is first homogenized thoroughly by vigorous shaking. Approximately 10 g sample is weighed, with a precision of 0,001 g, into a 100 ml PE bottle (5.1) and diluted with kerosene (4.2) up to a weight of approximately 20 g, with a precision of 0.001 g. Calculate the exact concentration, taking into account the exact weights. The resulting mixture is thoroughly homogenized by shaking. The exact dilution factor, DF (see 7.1), which is nominally 2,000 (20,000 g/10,000 g), is calculated and saved for the calculations in clause 10.

NOTE The reason for using the amount of kerosene listed in this clause instead of using paraffin oil as described for calibration is the attempt for minimization of differences in viscosity.

9.2 Measurement

The analysis of Ca and Mg and of Na and K is performed according to the instructions of the ICP manufacturer, using the wavelengths indicated in clause 5.3. For the measurement of Na and K, it is strongly recommended to take at least three readings from independent aspirations of the sample, of which the arithmetic mean is used as a single determination.

10 Calculation

The content of each element under investigation is calculated from the resulting signals by use of the inverse of the calibration function, taking into consideration the dilution factor, DF, which has been actually used in the measurement. This can be done either manually, or with use of the appropriate software functions of the ICP OES spectrometer. The sum of the contents of Calcium and Magnesium and the sum of the contents of Sodium and Potassium shall be calculated from the un-rounded contents of the corresponding single elements. When the content of one element is below the scope of the method (< 1 mg/kg), the content of the element is not considered in the calculation of the sum.