SLOVENSKI STANDARD
SIST EN 15944:2011

01-januar-2011

Tekoči naftni proizvodi - Določevanje niklja in vanadija - Optična emisijska spektrometrija z induktivno sklopljeno plazmo (ICP OES)

Liquid petroleum products - Determination of nickel and vanadium content - Inductively coupled plasma optical emission spectrometry (ICP OES)

Flüssige Mineralölerzeugnisse - Bestimmung des Gehaltes an Nickel und Vanadium - Induktiv gekoppeltes Plasma Optisch-Emissionspektrometrisches direktes Prüfverfahren (IGP-OES)

Produits pétroliers liquides - Détermination de la teneur en nickel et vanadium - Méthode spectrométrique optique directe par plasma à couplage inductif (SOD-PCI)

Ta slovenski standard je istoveten z: **EN 15944:2010**

ICS:

75.080	Naftni proizvodi na splošno	Petroleum products in general

SIST EN 15944:2011 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15944

November 2010

ICS 75.100

English Version

Liquid petroleum products - Determination of nickel and vanadium content - Inductively coupled plasma optical emission spectrometry method (ICP OES)

Produits pétroliers liquides - Détermination de la teneur en nickel et vanadium - Méthode directement par spectrométrie d'émission atomique à couplage inductif par plasma (SOD-PCI)

Flüssige Mineralölerzeugnisse - Bestimmung des Gehaltes an Nickel und Vanadium - Optische Emissionsspektralanalyse mit induktiv gekopppeltem Plasma (ICP OES)

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Ref. No. EN 15944:2010: E

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Foreword

This document (EN 15944:2010) 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of an identical text or by endorsement, at the latest by May 2011, and conflicting national standards shall be withdrawn at the latest by May 2011.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

The method described in this document is based on DIN 51790-6 [1]. It has been developed originally as an alternative to (second part of) EN 13131 [2], but as the method enables the use of an instrumental technique more and more employed in analytical laboratories, it was decided to have it as a stand-alone method.

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, Croatia, 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 the United Kingdom.

1 Scope

This European Standard specifies an inductively coupled plasma optical emission spectrometry (ICP OES) method for the determination of nickel content in the range 4 mg/kg to 55 mg/kg and of vanadium content in the range 4 mg/kg to 150 mg/kg in fuel oils and residual fuel oils.

NOTE 1 Nickel content can be determined from 2 mg/kg to 4 mg/kg and vanadium content can be determined from 1 mg/kg to 4 mg/kg. However, the precision was not established as no samples with nickel and vanadium contents in these ranges were included in the interlaboratory test. Nickel and vanadium contents higher than those reported can be determined after sample dilution. However, the precision was not established for diluted samples.

NOTE 2 For the purposes of this European Standard, the term "% (*V/V*)" is used to represent the volume fraction (φ).

WARNING — The 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 1042, *Laboratory glassware — One-mark volumetric flasks (ISO 1042:1998)*

EN ISO 3170, *Petroleum liquids — Manual sampling (ISO 3170:2004)*

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

3 Principle

The sample is diluted with an organic solvent. The solution is then introduced directly into the ICP OES spectrometer. Vanadium and nickel contents are determined by comparison with calibration solutions. An internal standard is employed to correct viscosity effects.

4 Reagents

4.1 Paraffin oil, with viscosity between 1,5 mm^2/s and 6,0 mm^2/s, 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 Xylene, analytical reagent grade.

4.4 2-Ethyl hexanoic acid, analytical reagent grade or other suitable stabilizer for element standard solution.

1) This information is given for the convenience of the 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.

4.5 Element standard solutions, dissolved in oil, for example with 500 mg/kg per element, available as single element standards, or at least partially as multi-element standards.

NOTE Some commercial element standard solutions on the market are furnished with higher content. Those solutions may be used instead of the required solutions, but an initial mass to mass dilution should be done according to recommendations given in 7.1.

4.6 Argon, with minimum purity φ(Ar) = 99,996 % *(V/V).*

NOTE Small amounts of oxygen (minimum purity $\varphi(O_2) \geq$ 99,995 % (*V/V*)) may be added to the argon gas stream using a metering valve (30 ml/min to 100 ml/min) to prevent carbon deposits in the area of the plasma torch.

5 Apparatus

5.1 Laboratory equipment

All glassware shall be cleaned carefully before use to remove soluble constituents. Fill new glass vessels with xylene (4.3) and allow to stand for at least two days.

5.1.1 Glassware

5.1.1.1 Beakers, tall type, 150 ml.

5.1.1.2 Erlenmeyer flasks with wide neck and plug, 50 ml.

5.1.1.3 Volumetric flasks, 500 ml, according to EN ISO 1042, with narrow neck and plug.

5.1.2 Sample containers, storage bottles with screw cap, brown glass.

5.1.3 Graduated pipettes or variable volume automatic pipettes, fitted with disposable polypropylene tips.

5.2 Balance, capable of weighing to the nearest 0,001 g.

5.3 ICP OES spectrometer, equipped with organic sample introduction system.

5.3.1 General

Simultaneous and equally suitable sequential ICP OES spectrometer equipped for the analysis of organic liquids, with a high-frequency generator and a nebulizer suitable for organic solvents. The use of a feed pump for sample introduction into the nebulizer is required. Both setup and operation of the ICP OES spectrometer shall be done in accordance with operating instructions of the manufacturer.

5.3.2 Recommended wavelengths

The recommended wavelengths for nickel, vanadium and internal standard element are reported in Table 1.

Organometallic yttrium has performed well as an internal standard for this test method and is recommended.

Table 1 — Recommended wavelengths

Element	Wavelength nm
Nickel	216,555 – 231,604 – 221,647
Vanadium	292,401 – 309,310
Cobalt Scandium Yttrium	238,892 361,383 224,306 – 371,029 – 360,073

NOTE The line at 227,021 nm may be used for nickel, but this line suffers from interference with tungsten. Lines at 268,796 nm and 311,070 nm may be used for vanadium, but these lines suffer from interference with molybdenum and manganese respectively.

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 the product under consideration.

The samples shall be filled into clean containers. The containers shall be rinsed with xylene (4.3) at least twice and then dried before use.

7 Preparation of calibration solutions

7.1 General

In order to avoid inhomogeneity, the standard solutions (4.5) shall be shaken vigorously before use.

The masses given correspond to a nominal element content of 500 mg/kg per element in the multi-element solutions (4.5). If solutions with other element contents or single element standards are used, these masses shall be adjusted accordingly in order to establish the given nominal concentrations as closely as possible. Calculate the exact concentrations of the calibration solutions, taking into account the exact masses.

7.2 Calibration solutions

For each calibration solution, weigh stock standard solution (4.5), stabiliser (4.4), and paraffin oil (4.1) to the nearest 0,001 g in 50 ml Erlenmeyer flasks (5.1.1.2) as indicated in Table 2. All solutions shall be homogenized by vigorous shaking.

Table 2 — Calibration solutions

Calibration solution	Element content mg/kg	Standard solution g	Stabilizer g	Paraffin oil g
1	0 (blank)	-	0,15	24,85
2	5	0,25	0,15	24,60
3	10	0,50	0,15	24,35
4	20	1,00	0,15	23,85
5	100	5,00	0,15	19,85
6	200	10,00	0,15	14,85

7.3 Internal standard solution

Weigh 5 g of cobalt, scandium or yttrium stock solution (4.5) with a precision of 0,001 g in a 500 ml volumetric flask (5.1.1.3).

Add 3 g of stabilizer (4.4) and fill up to 500 ml with a mixture of kerosene/xylene solvent having a volume ratio of 2:1 (4.2 and 4.3).

The solution shall be homogenized before use by vigorous shaking.

NOTE 1 The use of a mixture of xylene and kerosene is necessary to avoid precipitation of asphaltene fractions occurring when kerosene only is employed, and to reduce the build-up of carbon on the tip of the torch.

NOTE 2 Experience from daily practice with yttrium used as internal standard has shown that internal standard solutions can be used for about two weeks.

7.4 Working solutions

For each calibration solution (7.2), weigh (1,0 ± 0,001) g in a 50 ml Erlenmeyer flask (5.1.1.2). Add 10 ml of internal standard solution (7.3).

All prepared solutions shall be homogenized by vigorous shaking.

8 Calibration

8.1 General

The ICP OES spectrometer setup with organic solutions and the instrument check are performed according to the instructions of the manufacturer.

The choice of the instrumental parameters is made to obtain the best signal/background ratio for all elements.

Net intensity of analytical lines shall be calculated by subtracting the intensity measured at appropriate background wavelengths. Some instruments are equipped with software which allows the automatic correction of the background. A separate calibration function for each element under investigation shall be established.

8.2 Calibration of the ICP OES spectrometer

The calibration of the ICP OES spectrometer shall be done by the measurement of the blank solution and of the working solutions (7.4) using three replicates. For the determination of the elements, the wavelengths recommended in Table 1 shall be used. The background subtraction shall be performed at wavelengths not affected by other lines.

IMPORTANT — Ensure that the wavelengths used in calibration also match exactly the ones used in the sample measurement.

Depending on the spectrometer software, follow either procedure A or B.

8.3 Procedure A

For each element under investigation, conduct the aspiration of the working solutions (7.4).

For each working solution, measure the net emission intensity of nickel, I_{Ni}, and of vanadium, I_V, and the net emission intensity of the internal standard, I_{IS}, at the chosen wavelengths.

Calculate the intensity ratio of nickel, R_{Ni}, and of vanadium, R_V, of each working solution using the following: