SLOVENSKI STANDARD
SIST EN 16476:2014

01-julij-2014

Tekoči naftni proizvodi - Določevanje natrija, kalija, kalcija, fosforja, bakra in cinka v dizelskem gorivu - Metoda z optično emisijsko spektrometrijo z induktivno sklopljeno plazmo (ICP-OES)

Liquid Petroleum products - Determination of Sodium, Potassium, Calcium, Phosphorus, Copper and Zinc contents in diesel fuel - Method via Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Flüssige Mineralölerzeugnisse - Bestimmung des Gehalts an Natrium, Kalium, Calcium, Phosphor, Kupfer, Zink in Dieselkraftstoffen - Direkte Bestimmung durch optische Emissionsspektrometrie mit induktiv gekoppeltem Plasma (ICP-OES)

Produits pétroliers liquides - Détermination des teneurs en Sodium, Potassium, Calcium, Phosphore, Cuivre et Zinc dans le gazole - Méthode par spectrométrie d'émission atomique à couplage inductif par plasma (ICP OES)

Ta slovenski standard je istoveten z: **EN 16476:2014**

ICS:

71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis
75.160.20	Tekoča goriva	Liquid fuels

SIST EN 16476:2014 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16476

May 2014

ICS 75.160.20

English Version

Liquid petroleum products - Determination of Sodium, Potassium, Calcium, Phosphorus, Copper and Zinc contents in diesel fuel - Method via Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES)

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Foreword

This document (EN 16476:2014) 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of an identical text or by endorsement, at the latest by November 2014 and conflicting national standards shall be withdrawn at the latest by November 2014.

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.

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Introduction

This document specifies a method for determining concentration of the six most essential ash forming elements. The number of six was chosen in order to limit the complexity of the test and to be able to determine a decent method precision. The six elements were specified by the vehicle manufacturers. The test provides additional information to the more common ash concentration determination methods which do aim towards filter problems. Metals have more impact on the durability of modern DPF exhaust gas after-treatment systems in diesel vehicles than ash in general.

1 Scope

This European Standard specifies an inductively coupled plasma optical emission spectrometry (ICP OES) method for the determination of sodium, potassium, calcium, phosphorus, copper and zinc concentrations of diesel fuels, including those containing up to 30 % (*V/V*) fatty acid methyl ester (FAME), in the range detailed in Table 1. These six elements are considered as the most essential ash forming elements.

Table 1 — Application ranges for ash forming elements

Element	Range mg/kg
Sodium	1,2 to 2,5
Potassium	0,9 to 2,5
Calcium	0,3 to 2,5
Phosphorus	0,9 to 2,5
Copper	0,2 to 2,5
Zinc	0,2 to 2,5

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

WARNING — The use of this European Standard may involve hazardous materials, operations and equipment. This European Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this European Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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)*

EN ISO 3170, *Petroleum liquids - Manual sampling (ISO 3170)*

EN ISO 3171, *Petroleum liquids - Automatic pipeline sampling (ISO 3171)*

3 Principle

A weighed amount of diesel fuel sample is diluted with an organic solvent. The solution is then introduced directly into an ICP OES spectrometer. Sodium, potassium, calcium, phosphorous, copper and zinc concentrations are determined by comparison with calibration solutions. An Internal Standard is employed to correct viscosity effects.

4 Reagents

If not specified otherwise, only chemicals of a known high degree of purity shall be used.

4.1 Kerosene, boiling range between 175 °C and 250 °C, elements free. The solvent shall contain less than 0,1 mg/kg of each of the element under test.

NOTE In case of unstable plasma or in case of special laboratory requirements, kerosene can be substituted by other suitable solvents, provided that they are free of analytes.

4.2 Sodium Standard solution, commercially available in oil, containing, e.g. 1 000 mg/kg sodium.

4.3 Potassium Standard solution, commercially available in oil, containing, e.g. 1 000 mg/kg potassium.

4.4 Calcium Standard solution, commercially available in oil, containing, e.g. 1 000 mg/kg calcium.

4.5 Phosphorus Standard solution, commercially available in oil, containing, e.g. 1 000 mg/kg phosphorus.

4.6 Copper Standard solution, commercially available in oil, containing, e.g. 1 000 mg/kg copper.

4.7 Zinc Standard solution, commercially available in oil, containing, e.g. 1 000 mg/kg zinc.

4.8 Sodium, potassium, calcium, phosphorus, copper and zinc intermediate working Standard (50 mg/kg each).

Weigh (1,00 g ± 0,01) g of each element Standard solution (4.2), (4.3), (4.4), (4.5), (4.6), (4.7) into a 50 ml bottle (5.2). Add kerosene (4.1) to (20,00 ± 0,20) g. Each mass shall be weighed to the nearest 0,001 g.

In the case of using several mono-element Standard solutions, attention shall be paid to ensure that they are free of other analyte elements.

Some commercial element Standard solutions are furnished with higher concentration on the market. Those solutions may be used instead of the required solutions, but in this case an initial mass to mass dilution shall be done according to recommendations given in 7.1.

Ready-made commercial multi-element Standard solutions may be used instead of the single element Standard solutions (4.2, 4.3, 4.4, 4.5, 4.6 and 4.7) as the method is designed to avoid interference at the wavelengths specified.

4.9 Internal Standard solution (cobalt, scandium, yttrium), commercially available in oil (analyte free), for example with 1 000 mg/kg per element, available as single element Standard.

NOTE The internal Standard solutions are commonly available as single element Standards with various element concentrations.

4.10 Argon, with a mass fraction w (Ar) ≥ 99,996 %.

Small amounts of oxygen may be added to the argon gas stream using a metering valve (for example 30 ml/min to 100 ml/min) to prevent carbon deposits in the area of the plasma torch.

5 Apparatus

5.1 Volumetric flasks, 25 ml and 250 ml, according to EN ISO 1042, with taper sleeve and plug.

To avoid contamination of the test samples, all solutions shall be prepared in plastic containers. Surfaces which can come in contact with the solutions shall not be touched by hand.

To avoid phosphorus contamination due to the phosphates contained in the detergents used for washing the flasks, rinse the latter at least twice with an approximate 5 mol/l solution of nitric acid. Then rinse with distilled water and dry.

The use of borosilicate glass containers is not recommended due to the risk of sodium contamination.

5.2 Bottles, 50 ml, with screw caps, polyethylene PE.

To avoid phosphorus contamination due to the phosphates contained in the detergents used for washing the bottles, rinse the latter at least twice with an approximate 5 mol/l solution of nitric acid. Then rinse with distilled water and dry.

5.3 Analytical balance, capable of weighing to the nearest 0,000 1 g.

5.4 ICP OES spectrometer

5.4.1 General

ICP OES spectrometer equipped for the analysis of organic liquids. The use of a feed pump for sample introduction into the nebuliser is required. Pump tubing shall be suitable for organic use. Both setup and operation of the ICP OES spectrometer shall be done in accordance with operating instructions of the manufacturer.

The use of vertically oriented plasma, radially observed ICP OES is recommended to avoid carbon residue formation and minimize matrix interference due to the presence of carbon in the plasma.

5.4.2 Recommended wavelengths

The recommended wavelengths of sodium, potassium, calcium, phosphorus, copper and zinc, cobalt, scandium and yttrium are given in Table 2.

Table 2 — Recommended wavelengths

Element	Wavelength [a] nm			
Sodium	589,592	588,995		
Potassium	766,491	769,897		
Calcium	317,933	184,006 (183,944)	315,887	396,847 393,366
Phosphorus	177,499 (177,434)	178,287 (178,222)	213,618[b]	214,914
Copper	324,754	327,396	224,700	
Zinc	206,200	213,856		202,548 [b]
Cobalt	238,892	258,033		
Scandium	361,383			
Yttrium	224,306	371,029	360,073	

[a] Wavelengths are expressed as vacuum lines or as air lines (in brackets) according to the expression of the different manufacturers of ICP OES spectrometers.

[b] Can be slightly interfered by Cu at the same wavelength.