SLOVENSKI STANDARD
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Tekoči naftni proizvodi - Goriva na osnovi srednjih destilatov, metilnih estrov maščobnih kislin (FAME) in mešanic - Medlaboratorijsko poročilo o uporabnosti oksidacijske preskusne metode rapidne male skale

Liquid petroleum products - Middle distillates and fatty acid methyl ester (FAME) fuels and blends - Round Robin report on applicability of Rapid Small Scale Oxidation Test method

Fettsäure-Metyl-Ester (FAME) als Kraftstoff und als Blendkomponente für Dieselkraftstoff - Ringversuchsbericht zur Anwendbarkeit des Verfahrens zur Bestimmung der Oxidationsstabilität mit beschleunigtem Verfahren und kleiner Probenmenge

Produits pétroliers liquides - Distillats moyens, carburants à base d'esters méthyliques d'acides gras (EMAG) et leurs mélanges - Rapport de l'essai interlaboratoires concernant l'applicabilité de la méthode d'oxydation accélérée à petite échelle

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Liquid petroleum products - Middle distillates and fatty acid methyl ester (FAME) fuels and blends - Round Robin report on applicability of Rapid Small Scale Oxidation Test method

Produits pétroliers liquides - Carburants et mélanges des distillats moyens et des esters méthyliques d'acides gras (EMAG) - Réport de Round Robin de l'application de la détermination methode d'oxydation accéléree petite échelle

Flüssige Petroleum Produkte - Mitteldestilat und Fettsäuremethylester (FAME) Kraftstoffen und Mischungen - Round Robin Rapport der Applikation des beschleunigten kleinen Maßstaben Oxidationstests

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Foreword

This document (CEN/TR 16366:2012) 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.

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This document presents background to EN 16091.

1 Scope

This Technical Report describes a series of round robin test campaigns for precision estimation of EN 16091. Furthermore, this document includes a summary of the results of the RRTs (see Clause 7 and Annex B).

NOTE The identities of the participating laboratories are not displayed in this report. They are, however filed with the original RRT documentation at the CEN/TC 19/JWG1 secretariat.

2 Test method background

The Rapid Small Scale Oxidation Test method (RSSOT[1], EN 16091, [1]) is developed as an additional or parallel test method for the determination of oxidation stability (EN 14112 [2] and EN 15751 [3]) in FAMEs according to EN 14214 [5] and diesel fuel – biodiesel blends [4].

Three precision studies (2007-231, 2008-231, 2010-231) have been executed in CEN/TC 19/JWG 1 in order to access the test method precision in terms of repeatability, *r,* and reproducibility, *R*.

NOTE In addition, more RR-testing has been executed in order to compare results with those from other tests like EN 14112, EN 15751 or acid number after ageing. These additional test results are not subject of this precision report but are reported elsewhere. It shall be noted that the Rancimat[2] and PetroOXY[1] results exhibit a good correlation, obviously indicating that both methods provide good estimations of oxidation stability.

The three precision studies (2007-231, 2008-231, 2010-231) contained the following:

— RRT 2007-231 → pre- study with 10 samples ("B2" .. "B30") in 5 laboratories;

— RRT 2008-231 → RRT with 23 samples ("B0" .. "B100") in 19 laboratories;

— RRT 2010-231 → RRT with 7 samples testing the influence of EHN in 11 labs (EHN = Cetane improver = 2-ethyl hexyl nitrate).

The draft version of EN 16091 was sent to the laboratories as the requested test procedure along with the Round Robin instructions. The same test method procedure was used is the three different RRTs. Since no significant modifications had been made which could be precision-relevant, this test procedure remained the same as specified in the final standard (EN 16091:2011).

3 Description of the samples

3.1 RRT 2007-231

There were 10 samples used for the pre-study in 2007. Each sample was randomized, blind coded and distributed by the coordinator of this RRT.

The following samples had been agreed by the CEN/TC 307/WG 1, 10 Bx samples: 1 x B2, 1 x B4, 1 x B5, 1 x B7, 1 x B8, 1 x B12, 1 x B15, 1 x B20, 1 x B30, 1 x B100. The samples have been prepared by blending of one B0 and one B100 (RME/SME (90/10)). Information of the fuel properties are not provided.

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1) Also known as the PetroOXY test. PetroOXY is the trade name of a product supplied by Petrotest, Instruments GmbH & Co, Germany. This information is given for the convenience of users of this European Technical Report and does not constitute an endorsement by CEN of the product named.

2) Rancimat is the trade name of a product, model 743, supplied by Metrohm AG, Switzerland and an example of suitable equipment available comercially. This information is given for the convenience of users of this European Technical Report and does not constitute an endorsement by CEN of the product named.

3.2 RRT 2008-231

There were 23 samples used for the RRT 2008-231. Each sample was randomized, blind coded and distributed by the coordinator of this RRT.

The following samples were agreed by the CEN/TC 307/WG 1, in addition to 4 B100 Samples 19 Bxx samples were used: 3 x B00, 6 x B05, 6 x B10 and 4 x B30. The 16 Bxx (B05, B10, B30) fuels have been prepared by blending of one B00 and one B100 without the addition of other products (additives).

The properties of B0 are given in Table 1.

Table 1 — Diesel Fuel B0 properties for the RRT 2008-231

Property	Unit	Method	Fuel 1[a] EN 590 fuel[d]	Fuel 2[b] EN 590 fuel[d]	Fuel 3[c] Swedish Class 1[d]
Sulfur Content	mg/kg	EN 20846	8,6	9,8	< 3
FAME Content	% (*V/V*)	EN 14078	0	0,2	0
PAC	% (*m/m*)	EN 12916	5,5	2,4	0,1

[a] Additised with lubricity- and CFPP improver — no cetane improver

[b] EHN (Ethyl – Hexyl – Nitrate) < 100 mg/kg (IR test method)

[c] No information

[d] The suppliers of these fuels are available from the Secretariat of CEN/TC 19/JWG 1.

The properties of FAME (B100) are given in Table 2.

Table 2 — FAME (B100) properties for RRT 2008-231

Parameter	Unit	Method	FAME A[a]	FAME B[a]	FAME C[a]	FAME D[a]
Composition			RME	RME	SME 75 % PME 25 %	RME 60 %
BHT	mg/kg	—	No	1 000	No	No
Oxidation stability	h	EN 15751	5,8	13,6	7,2	6,0

[a] The supplier of all FAMEs is available from the Secretariat of CEN/TC 19/JWG 1.

The sample identification is given in Table 3.

Table 3 — Samples identification RRT 2008-231

Sample Number	Fuel Type	Sample Code	Diesel fuel used	FAME used	FAME content (% (*V/V*))
S1	B100	FAME A	—	—	100
S2	B100	FAME B	—	—	100
S3	B100	FAME C	—	—	100
S4	B100	FAME D	—	—	100
S5	B10	G1A10	1	A	10
S6	B30	G1A30	1	A	30
S7	B5	G1A5	1	A	5
S8	B10	G1B10	1	B	10
S9	B30	G1B30	1	B	30
S10	B5	G1B5	1	B	5
S11	B10	G1C10	1	C	10
S12	B30	G1C30	1	C	30
S13	B5	G1C5	1	C	5
S14	B10	G1D10	1	D	10
S15	B30	G1D30	1	D	30
S16	B5	G1D5	1	D	5
S17	B10	G2B10	2	B	10
S18	B10	G2A10	2	A	5
S19	B5	G2C5	2	C	5
S20	B5	G2D5	2	D	5
S21	B0	Fuel No.1	—	—	—
S22	B0	Fuel No.2	—	—	—
S23	B0	Fuel No.3	—	—	—

3.3 RRT 2010-231

There were in origin 7 samples in the RRT 2010-231: 5 x B0 samples without Ignition Improver.

The suppliers of these fuels are available from the secretariat of CEN/TC 19/JWG 1. All B0 samples meet the requirements of EN 590. The properties are given in Table 4.

Table 4 — Diesel fuels B0 properties

Property	Unit	Method	B01[a] Swedish Class 1	B02[a] EN 590	B03[a] EN 590	B04[a] EN 590	B05[a] EN 590
Sulphur	mg/kg	EN 20884	< 1	N/A	4,7	< 3	12
FAME	% (*V*/*V*)	EN 14078	< 0,05	N/A	< 0,1	< 0,1	< 0,5
PAH	% (*m*/*m*)	EN 12916	0,1	N/A	4,8	1,4	2,1
IBP	°C	ISO 3405	N/A	N/A	189	207,9	200,1
T95	°C	ISO 3405	284	N/A	363	327,3	352,2
Flashpoint	°C	EN 2719	72	N/A	80,5	85	81,5
[a] The suppliers of these fuels are available from the secretariat of CEN/TC 19/JWG 1.							

In addition two B7 samples were used. One from a local station and one based on the B04 EN 590 sample blended with RME up to a content of 7 % RME.

The B0 and B7 samples were prepared with different concentrations of EHN (EHN = Cetane improver = 2-ethyl hexyl nitrate), and the following sample set was used in eleven labs (see Table 5).

Table 5 — Sample set used

FUEL	EHN 0 mg/kg	EHN 500 mg/kg	EHN 1000 mg/kg
B01	X	X	X
B02	X	X	X
B03	X	X	X
B04	X	X	X
B05	X	X	X
B7-1	X	X	—
B7-2	X	X	—

In total, there were 19 samples. Each sample was randomized, blind coded and distributed by the coordinator of this RRT.

For each RRT and laboratory participant a verification fluid from the manufacturer was sent to check if the used instruments were in the limit of a given oxidation stability value.

4 Round Robin Instructions

The test program instructions were sent to each participating laboratory (see Annex A).

5 Description of equipment

The apparatus used by each laboratory in this study to develop a precision statement was the Petrotest, model PetroOXY[1)].

6 Form of data reports

Each laboratory was provided with a data report form for collection of data. The filled out data report forms were sent by the laboratories to the coordinator of these RRTs.

7 Statistical data summary

All precision values have been calculated following the procedures in EN ISO 4259 [6]. For the final precision statement in EN 16091, the results from RRT 2008-231 and 2010-231 were combined, resulting in the following precision formulae:

$$r = 0{,}288X + 0{,}496\,5 \quad (1)$$

$$R = 0{,}086\,3X + 1{,}377\,2 \quad (2)$$

where

r is the repeatability (the difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material);

R is the reproducibility (the difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material);

X represents the mean of the two results expressed in min, rounded to the nearest 0,01 min.

Some more statistical detail and data is given in Annex B. The statistical review was provided by several precision experts of DIN FAM (Fachausschuss Mineralöl- und Brennstoffnormung des NMP (FAM)).

Annex A
(informative)

Comparative study protocol for oxidation stability test methods

IMPORTANT — Before starting sample measurements, read this protocol carefully and follow the instructions.

A.1 Scope and overview

The main purpose of this CEN Round Robin is to determine the precision of three proposed 'Oxidation Stability' test methods: EN 15751 (Rancimat[2)]) method, JAMA (Delta Acid Number) method and PetroOXY[1)] method. A second objective is to determine if any correlations exist between any of the measured properties of the methods.

The specific consideration of this study is to find a useful method which is able to predict the oxidation stability for pure mineral oil diesel (B0) and different bio-diesel blends (B5, B10, B30). The Rancimat and PetroOXY methods will also make measurements on pure FAME (B100) materials.

Precision will be determined in accordance with EN ISO 4259. The correlations between methods will be determined by additional statistical means.

A.2 Round Robin sample reception

Along with the PetroOXY test method protocol (dated XX/XX/XX) you will receive:

— a set of 23 samples with unique codes;

— 50 plastic pipettes;

— 100 O–ring seals;

— 1 Petrotest verification fluid;

— an instruction manual.

You will be provided with a unique laboratory code to preserve confidentiality. The laboratory code and the designated sample number and its origin are known only to the round robin programme coordinator.

A computer programme has randomly generated the testing order and no two laboratories have the same order. Upon receipt of the samples, please do the following:

— unpack the samples from the box;

— check the samples containers for any signs of damage or leakage;

— if there is any, please contact the programme manager and add all information indicated on the label glued to the sample container;

— as soon as possible, store the samples away from direct sunlight and less than +25 °C is recommended.