SLOVENSKI STANDARD
SIST-TP CEN/TR 16885:2015

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Tekoči naftni proizvodi - Preiskovanje preskusne metode za merjenje oksidacijske stabilnosti dizla in FAME/dizelske mešanice s kislinskim številom po staranju

Liquid petroleum products - Investigation on test method for measurement of the oxidation stability of diesel and diesel/FAME blends by Acid Number after ageing

Flüssige Mineralöl-Erzeugnisse - Bericht über die Bestimmung der Oxidationsstabilität von Diesel und Diesel/FAME-Mischungen durch Bestimmung der Säurezahl nach Verälterung

Produits pétroliers liquides - Recherche de la détermination de la stabilité à l'oxydation du gazole et des mélanges gazole/EMAG par l'indice d'acide après vieillissement

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Flüssige Mineralöl-Erzeugnisse - Bericht über die Bestimmung der Oxidationsstabilität von Diesel und Diesel/FAME-Mischungen durch Bestimmung der Säurezahl nach Verälterung

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European foreword

This document (CEN/TR 16885:2015) 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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1 Scope

This Technical Report describes the investigation into the development of a standard test method to determine oxidation stability of diesel fuel and fatty acid methyl ester (FAME) blends in diesel by the use of determining the acid number after ageing at elevated temperature. It provides conclusions following this work that have been discussed by CEN. The result thereof is that no European Standard has been developed.

2 Context and creation of a dedicated subgroup

In case of poor diesel or biodiesel quality, ageing of the fuel in the fuel system under high pressure and temperature (recirculation of fuel, high injector temperature, long storage in the vehicle fuel tank) may cause various car problems due to the formation of acidity through oxidation (i.e. deposit of sediments, deposit of lacquer, corrosion, lube oil deterioration).

Acidity of the fuel is therefore considered as a relevant parameter to evaluate oxidation stability of the Diesel fuel. Test methods based on the measurement of the acid number (AN) after an ageing step were studied. An ageing test temperature of 115 °C which is significantly higher than the test temperature of 95 °C applied in EN ISO 12205 [1] has been chosen because it better discriminates fuel's oxidation stability. Additionally, it is closer to the temperature range prevailing in fuel systems of current and future engine technologies (i.e. common rail systems).

Customer complaints related to fuel degradation linked to oxidation stability in France are shown in Figure 1.

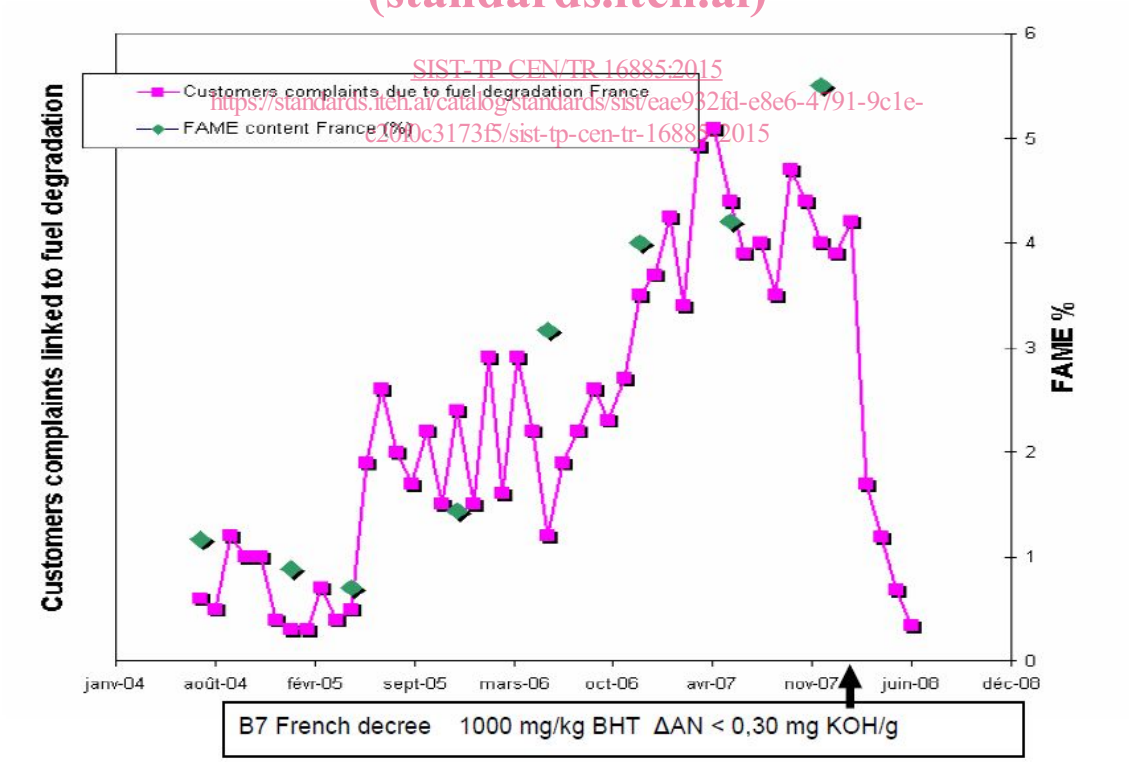


Figure 1 — Customer complaints linked to fuel degradation in France

A test method based on the change of the acid no. of a fuel during ageing, Delta AN, was evaluated in CEN/TC 19/JWG1 'FAME Test methods' in 2008. In the Delta AN method, the fuel is aged at 115 °C for 16 h by passing a stream of oxygen through the fuel using the oxidation cell of EN ISO 12205. The acid number of the fuel before ageing is subtracted from the acid number of the aged fuel. The results of Round Robin tests made on the Delta AN method led to the conclusion that the Delta AN test method, although discriminative, exhibits a precision not enough robust ; this test method needed some analytical improvements. A draft report about the test results applying the Delta AN method performed in 2008 was presented to CEN/TC 19/JWG1 in January, 2011.

Further work concerning the improvement of the Delta AN test method was carried out in France in 2009. A new test method based on the measurement of the acid number of the fuel after ageing was developed. Based on the results of a cross check test, it was decided at the JWG1 meeting on September 4, 2009, that additional work would be necessary concerning the robustness and precision of the new method. As such work being not covered by the CEN/TC 19 mandate to JWG1, it was proposed that experts continue the improvement work and issue a proposal for a NWI to WG 24.

Based on the results of the work of the French experts the continuation of the work was accepted by WG24 in March 2010. JWG1 started the work, creating a dedicated subgroup for this preliminary new work item (PNWI).

3 Participants in the work

Several European experts were active within this project, represented by one or more member(s) participating in the meetings. The memberships are listed in Table 1.

Table 1 — Members of the Subgroup „Acid No.“

Company	Country	*Members*
PSA	France	P. Jestin
TOTAL	France	S. Duperrier; P. Manuelli; P. Pestiaux; A. Vincent; A. Gandubert
SHELL	Germany	M. Schmidt
Deutsche BP	Germany	W. Strojek
Neste Oil	Finland	M. Kuronen
IFPEN	France	L. Pidol
OMV	Austria	W. Koliander
ADM	Germany	J. Groos; J. Fischer
ASG	Germany	T. Wilharm
Metrohm	Switzerland	C. Haider; U. Loyall
SGS	Germany, France	M. Kulikowski; D. Juillet

4 Meetings of the subgroup „Acid No.“

The members of the group have been working on the assessment of the oxidation stability of diesel and diesel/FAME blends by determination of the acid value after ageing from beginning of 2010 to mid-2014. The meetings are listed in Table 2. This work have been reported and discussed within JWG1 at each session. The main orientations and action plans have systematically been validated by JWG1.

Table 2 — Meetings of the Subgroup „Acid No.“

Meeting	Date and location
Meeting 1	April 27, 2010 Conference call
Meeting 2	July 07, 2010
Meeting 3	January 14, 2011
Meeting 4	May 24, 2011 PSA Peugeot Citroën – Paris
Call conference	July 25, 2011 Conference call
Meeting 5	September 02, 2011 IFPEN – Rueil
Meeting 6	March 22, 2012 PSA Peugeot Citroën – La Garenne Colombes
Meeting 7	November 13, 2013 TOTAL – Paris La Défense

5 Main steps of the work item study

5.1 Creation of the NWI

The first meeting of the group took place in April, 2010. The scope was presented to the members: the objective was to improve the precision of the new acid number test method applicable to diesel fuels from B0 to B10. In that context, some adjustments were made on the test method protocol and it was decided to run first a cross-check test. Necessary improvements based on the outcome of the study should be implemented to the method. A Round Robin test should finally be conducted in order to develop the precision of the method.

5.2 Test method used

The method used has been developed to be applicable to diesel fuels from B0 to B10. The main analytical parameters are listed hereafter and the full description of the test method is given in Annex A.

— Sample amount: (10 ± 0,2) g;

— Heating bath temperature: (115 ± 0,2) °C[1];

— Oxygen rate: (1 ± 0,1) L/h;

— Running time for fuel oxidation: 16 h ± 5 min;

— Maximal time between the end of oxidation step and the AN measurement: 4 h.

[1] The fuel was aged either in an oil bath or an heating bath as applied in the Rancimat equipment

5.3 First Round Robin Test

A RT was run in October, 2010 to assess the precision of the proposed new AN method on both colorimetric and potentiometric determination of the AN. Nine samples were used for the RRT: 3 B0, 4 B7 and 2 B10. Samples were representative for the European Market, some containing cetane improver (content between 100 and 1000 ppm), CFPP additives and/or lubricity additives. Thirteen labs out of fourteen participants have returned their results on time: ten labs have performed colorimetric determination (oil bath and Rancimat bath according to EN 15751 [2]) and eleven labs have performed potentiometric determination (oil bath and Rancimat bath according to EN 15751). The results of this RRT are given in Annex B.

The RRT results led to the following comments:

— Even if there was a discrimination between “good” and “bad” products, results were worse than expected, in particular for the potentiometric version. When the dispersion of results with the potentiometric method was discussed, all participants agreed that experimental parameters were perhaps not optimized and that it was necessary to work on it (electrode system, solvent, dynamic titration, etc.).

— “Home-made” diesels, meaning diesels formulated by blending “good” and “bad” B0 or B7 in order to reach certain AN target, seemed to have a strange behaviour. Even if the formulated products seemed to be homogeneous, the results obtained by the labs were really different and the statistical distribution of results indicated strong issues.

— There were some difficulties of being more precise on very good samples (AN <0,1 mg KOH/g). For non acidic samples, the resulting precision is poor due to the precision of colorimetric titration (in test method ISO 6618 [3] the reproducibility is 0,04 mg KOH/g for samples with AN <0,1 mg KOH/g).

— No impact of Rancimat bath compared to oil bath was observed, no bias was observed.

Thus this RRT pointed out that the method could not be used in the current state to be submitted for standardization. It was decided to continue the work to understand potentiometric results, to identify what could have an influence on the results dispersion and thus improving the method (work on experimental parameters, propose a few tests to assess the new parameters, …).

In parallel, the group members have decided to ask CEN/TC 19/WG 36 (statisticians) how a pass/fail test could be established, as this method could be considered as such.

All the details about this RRT are available in the internal document “Round Robin Study Report 2010-831” of CEN/TC 19.

5.4 Improvement of the test method

In order to improve the potentiometric titration test method, the participants of the first RRT were asked for detailed information of settings and conditions of their instruments. While there was no significant difference on the equipment (brand of device, software, electrode system, analytical parameters), the way of detection of the equivalent point was not the same for all participants. Indeed, the determination of the equivalent point can be automatically or manually done and some labs used the point corresponding to the pH 11 aqueous buffer. In parallel, several tests were performed by TOTAL to estimate the impact of various analytical parameters. Based on these results, some improvements were found to optimize the titration step:

a) Set all titration program parameters as proposed;

b) Use the colorimetric solvent and add indicator solution (to follow the solution colour change, especially for blank titration);

c) Perform a manual (re)check on equivalent point for each titration;

d) Do NOT use the point corresponding to the pH 11 aqueous buffer (to define the KOH sample volume).

At that stage of the study, the group decided organizing a new RRT with a well-defined measurement parameters for this RRT in order to minimize the variations from one lab to another. Nevertheless, all the experts agreed on the fact that the critical part of the test lies in the ageing step more than in the acid number determination.

5.5 Pass/fail methodology

The results obtained during the first RRT showed that it would be very difficult to propose a method with "classical" precision according to EN ISO 4259 [4] (*r* and *R* versus acid number). Indeed, the acid numbers measured on the RRT samples were not evenly distributed. The AN were either low or high and the samples formed two separate populations that can be considered as "good" samples and "bad" samples. By consequence, the members of the Subgroup proposed to use the preliminary tests on 44 B0 to B10 samples, conducted in August 2011, for the development of a Pass/Fail method. This model, developed in close cooperation with WG 36 experts, is based on General Discriminant Analysis (GDA). GDA applies the methods of the general linear model to the discriminant function analysis problem. It is a strong tool for detecting the variables that allow to discriminate between different groups, and for classifying samples into different groups with an accuracy better than chance.

In the two-group case, discriminant function analysis can be thought of as a special kind of multiple regression. If we code the two groups in the analysis as P (pass) and F (fail) and use that variable as the dependent variable in a multiple regression analysis, we would then get results that are analogous to those we would obtain via Discriminant Analysis. In general, in the two-group case a linear formula of the type:

$$\text{Group} = a + b_1{*}x_1 + b_2{*}x_2 + \ldots + b_m{*}x_m \quad (1)$$

where:

a is the constant

b_1 - b_m are regression coefficients

The interpretation of the results of a two-group problem is straightforward. Those variables with the largest (standardized) regression coefficients are the ones that contribute most to the prediction of group membership. Another major purpose to which discriminant analysis is applied is the issue of predictive classification of cases. Once a model has been finalized and the discriminant functions have been derived, we can predict to which group a particular sample belongs. The classification functions can be used to determine to which group each case most likely belongs. There are as many classification functions as there are groups. The classification functions can be used to directly compute classification scores for some new observations. Once the classification scores for a case are calculated it is easy to decide how to classify the case: in general the case is classified as belonging to the group for which it has the highest classification score.

Another important item is the probability that a new sample will make the predicted choice. Those probabilities are called posterior probabilities and are defined as the probability, based on the knowledge of the values of other variables that the respective case belongs to a particular group. Posterior probabilities can be used to evaluate the risk of a bad classification. In the case of the pass/fail two group classification with less than 0,95 or 0,99 probability should be disregarded. Like in regression models, a model needs to be validated on new samples not used for the model fitting.

In order to determine the feasibility of a pass/fail methodology for the determination of AN after ageing on Bx, the group members selected a set of 44 samples, from B0 to B10 (14*B0, 2*B5, 14*B7, 1*B8 and 13*B10), the preliminary test was run in August 2011. All the samples were analyzed by one laboratory (TOTAL). The results were processed by applying the General Discriminant Analysis leading to the classification of each sample as Pass or Fail. Figure 2 shows the results of the preliminary tests.

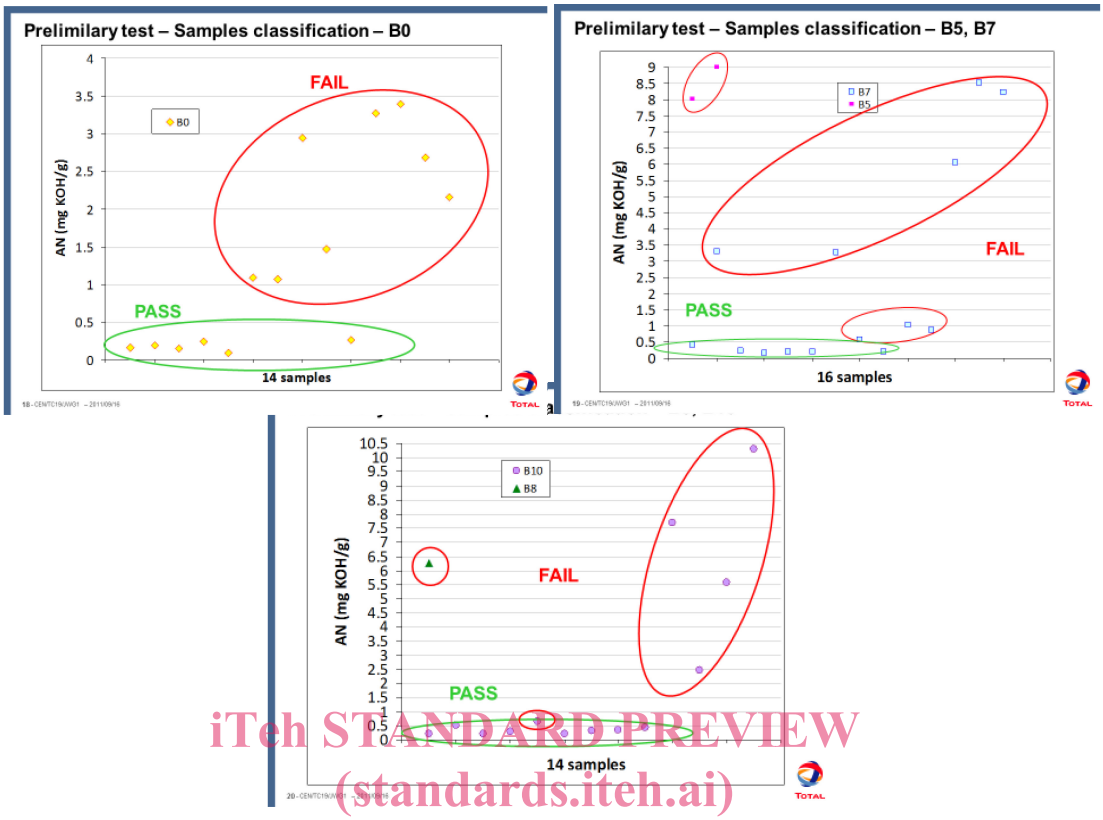


Figure 2 — Results of preliminary pass-/fail evaluation

Those preliminary tests were satisfying so the group decided to run a full Round Robin Test in agreement with CEN/TC 19/JWG1. Details are given in Annex C.

5.6 Second Round Robin Test

The RRT was performed by using the new AN method with AN measurement by potentiometric titration on 19 diesel blends (Bx). Those samples were either taken directly from European filling stations and refineries or formulated by blending B0 with FAME. In order to encourage labs' participation, it was proposed running the RRT in two parts in order to spread the workload for participants. The approach was agreed on by JWG1. Part 1 was launched in December 2012 and part 2 in February 2013. Seven laboratories out of eleven have provided full sets of results.

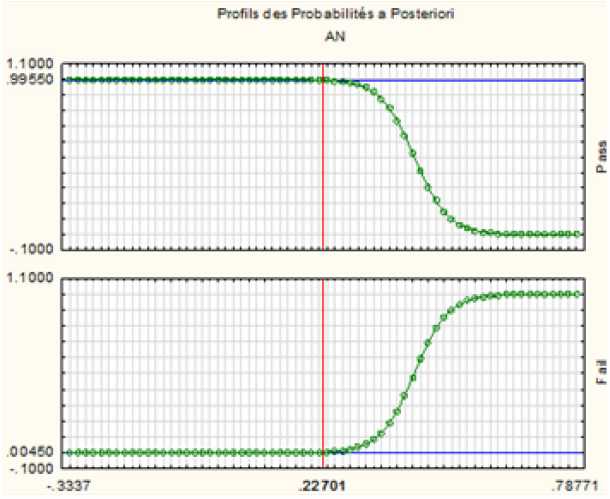
a) EN ISO 4259 approach

The evaluation of the data confirmed the result of the 2010 RRT: it was impossible achieving a precision which would have been acceptable for a standardized test method. Repeatability and reproducibility according to EN ISO 4259 [4] were not sufficient, the 2R criteria being not fulfilled for most of the samples (Annex B).

b) Pass-/Fail model

The model was improved by processing data of the Round Robin and the data of the preliminary using a AN threshold of 1,0. Details of the data evaluation (including the characterization of the sample aspect after ageing) are shown in Annex C. In contrary to the classical approach, processing the data by using the Pass/Fail model lead to robust classification functions and allowed the group to confirm the performance of the model on the new AN method. The classification functions ("ax + b" type) are the following ones:

	PASS	FAIL
a	-0,480 096	-11,942 8
	4,584 223	31,289 8



X axis : AN value based on the classification model
Y axis : a posteriori probability to belong to the concerned group

The classification of an unknown sample can be executed according to the following protocol:

— Measure AN after ageing;

— Calculate Pass and Fail criteria;

— The highest criteria gives the classification.

EXAMPLE

AN = 0,3 mgKOH/g Pass criterion = 0,894 270 9Fail criterion = 2,555 86

Sample is classified as PASS.

AN = 0,8 mgKOH/g Pass criterion = 3,186 382 4Fail criterion = 13,089 04

Sample is classified as FAIL.

Based on the evaluation of the results according to the described protocol the pass-/fail methodology seems to be robust and can distinguish between “good” and “bad” fuels; this was also confirmed by CEN/TC 19/WG 36 experts. The method can therefore be regarded as “validated” as a Pass/Fail method to determine the oxidation stability of diesel fuels which were experimentally covered by the discriminant analysis. A safe application of this method to fuels of unknown origin is not possible.

The best configuration was a discriminant analysis with a AN threshold of 1,0 (23 samples). Details of the construction of the pass/fail model are shown in Annex C.

All the details of this RRT are available in the internal CEN/TC 19 document “Round Robin Study Report 2013-460”.