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

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National foreword

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

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

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

This Technical Report was approved by CEN on 17 August 2015. It has been drawn up by the Technical Committee CEN/TC 19.

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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.

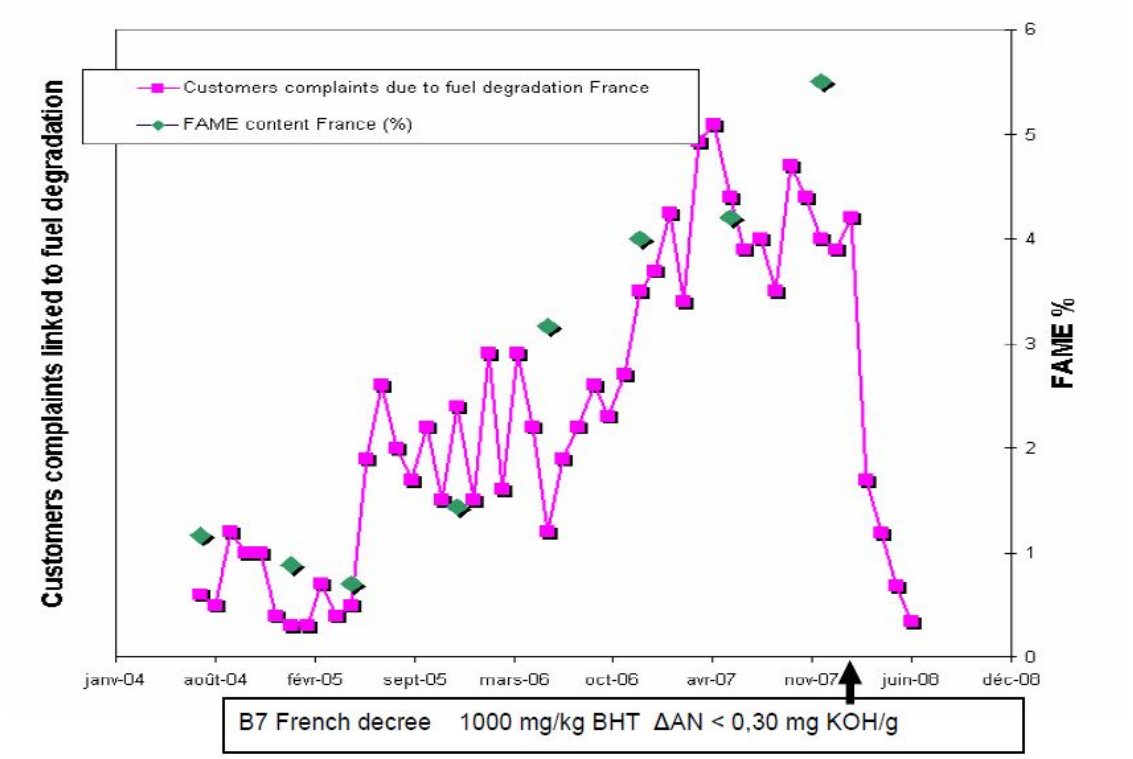


Figure 1 — Customer complaints linked to fuel degradation in France

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.

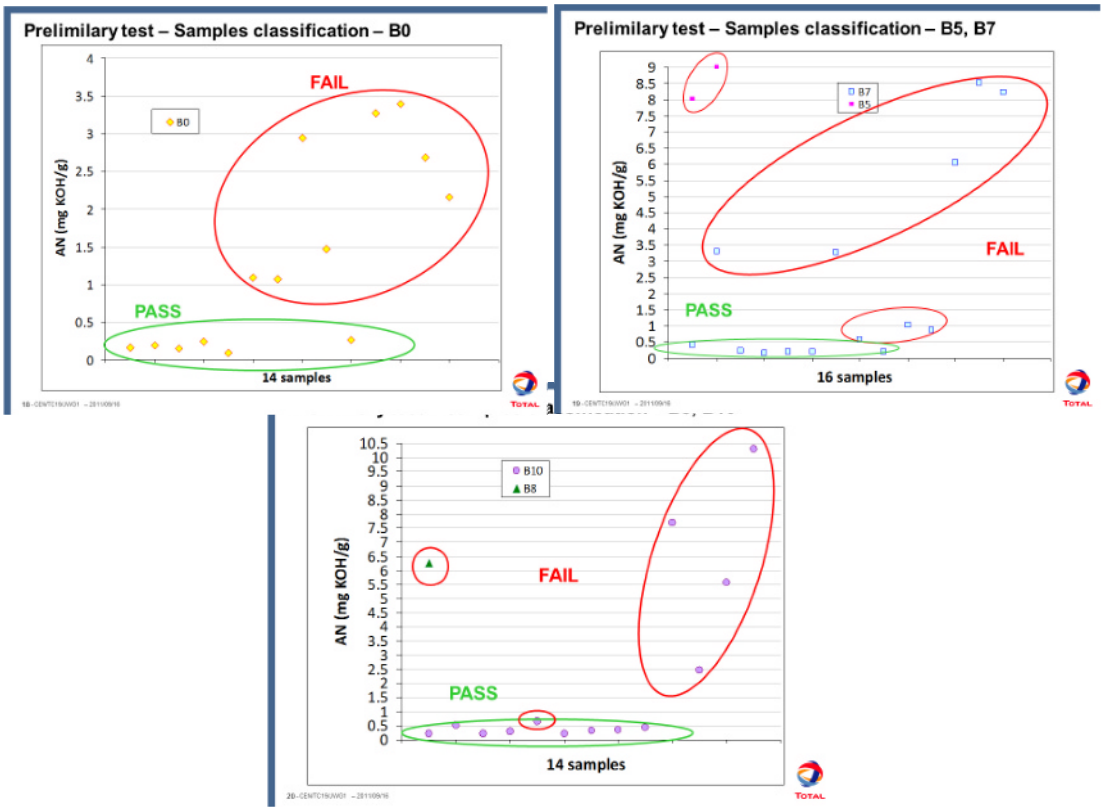


Figure 2 — Results of preliminary pass-/fail evaluation

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.

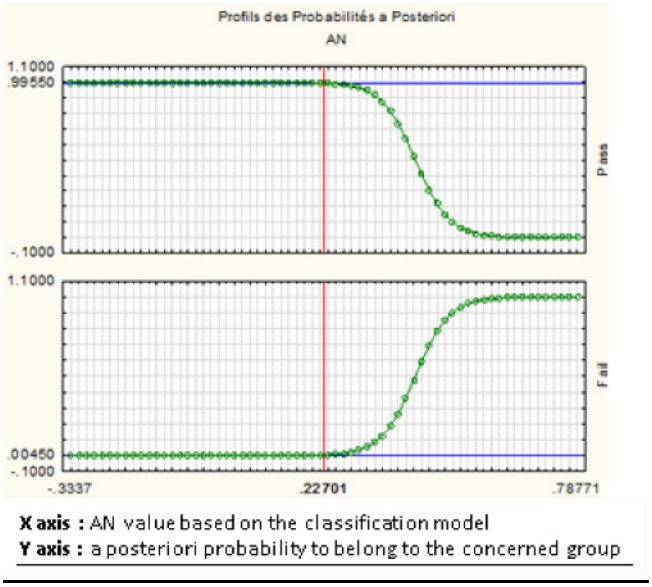
a) EN ISO 4259 approach

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



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”.

6 Conclusions

In spite of all efforts and valuable work for improving the measuring part, the method still shows a number of "defects" which would be very difficult to handle:

— the investigation if/if not real samples from the field would follow the same Pass/Fail population as the ones used in test method development,

— the question if there would be sufficient separation between the Pass and Fail sections in order to avoid errors in the pass/fail declaration,

— the potential need for a grey zone, where a pass/fail decision cannot be made with sufficient safety.

As it seems to be impossible to overcome these issues within a reasonable time the group concluded that for the time being there is no progress to foresee. Based on this information CEN/TC 19/JWG1 decided to apply to CEN/TC 19 to cancel the PNWI for the development of this method and to disband the subgroup. The new ageing method will not be submitted to CEN as EN method.

7 Acid number determination method available for lab use

The new AN method is described in Annex A and laboratories are free to use it to evaluate the PASS/FAIL criteria on their Bx samples, from B0 to B10.

8 Acknowledgements

Thanks to all the experts who have taken part to the work on the AN method during several years.

Thanks to the RRTs participants for their valuable activity in carrying out the analytical measurements.

Thanks to the companies for having supplied several batches of fuels and FAME.

Thanks to T. Feuerhelm, DIN FAM, and P. Pestiaux, TOTAL, for their comprehensive statistical evaluations.

Annex A
(informative)

Test method transcription

This annex is a copy of the test method for the measurement of the oxidation stability of Bx by Acid Number after ageing at 115 °C using potentiometric titration

1 Scope

This test method covers the measurement of the inherent acidity of diesel fuel and diesel fuel containing FAME under specified oxidizing conditions at 115 °C.

2 Referenced documents

ASTM D664, *Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration*

EN ISO 3696, *Water for analytical laboratory use – Specification and test method (ISO 3696)*

3 Terminology

Acid number: the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate a sample to a specified end point.

4 Summary of Test Method

10 g of sample are aged at 115 °C for 16 h while pure oxygen is bubbled through the sample at a rate of 1L/h in a long glass tube. After ageing, the flask is plunged into a bath containing ice and water to stop the oxidation. The sample is left at room temperature (20 °C to 25 °C) at least 1 h in the dark. The aged sample aspect is determined through visual inspection (clear and bright, hazy, etc.) and the acid number (AN) is measured according to a method based on the principle of test method ASTM D664: the sample is dissolved in a titration solvent and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a reference electrode or a combination electrode.

5 Apparatus

5.1 Ageing of the sample

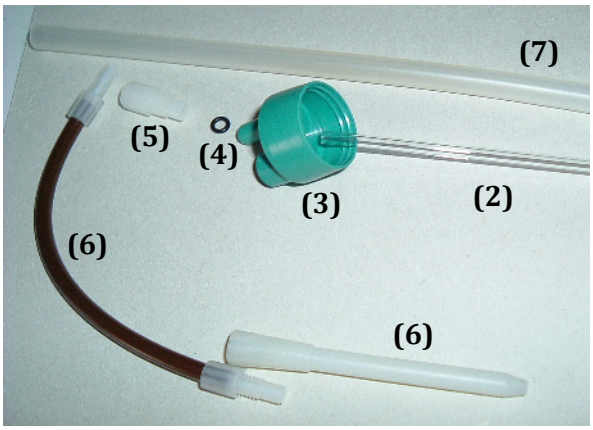
- *Heating bath (oil)*, shall be capable of maintaining the bath temperature at (115 ± 0,2) °C.

NOTE 1 The bath temperature is a key parameter of the oxidation reaction. It is thus advised to give specific care to the bath metrology (accuracy, stability and homogeneity of the temperature).

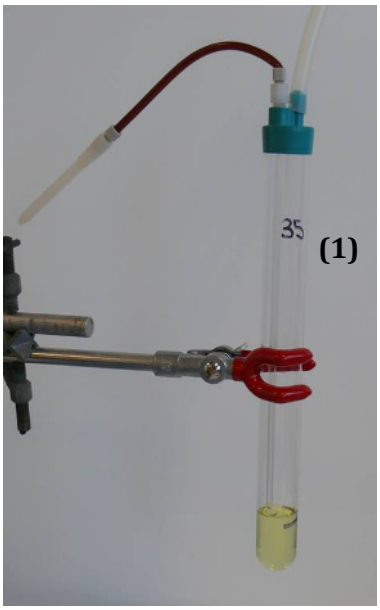
- *Flowmeters,* shall be capable of measuring an oxygen rate of (1 ± 0,1) L/h.
- Oxidation cell [2]:
    - Glass tube: L = 250 mm, external diameter = 24 mm (1)

[2] Equivalent to that of method EN 15751.

- Oxygen delivery tube (2)
- Tube cap (3)
- Ring (4)
- Connectors (5)
- Main oxygen delivery tube (6)
- Exhaust gas tube (7)



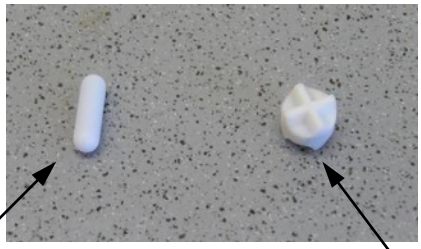
Used parts



Assembled oxidation cell

NOTE 2 The cleaning procedure for oxidation cells is described in appendix 1.

- *Magnetic stirrer*
- *Magnetic stirring bar*



L = 15 mm, diameter = 4,5 mm diameter = 8 mm

(more efficient when a red phase occurs after oxidation)

5.2 Measurement of acid number

Manual / automatic Titration Apparatus: see section 6 of ASTM D664.

Electrode System: see section 8 of ASTM D664.

Standardization of Apparatus: see section 9 of ASTM D664.

6 Reagents and materials

6.1 Ageing of the sample

- Reagent grade chemicals shall be used in all tests
- *Oxygen,* 99,5 % purity or better
- *Cleaning solvents* (technical grade):
  - Glassware:
    - solvent: toluene, isopropanol and water in the ratio 50/49.5/0.5
    - acetone
  - Plastic parts: propan-2-ol, water

6.2 Measurement of acid number

- Reagent grade chemicals shall be used in all tests
- *Water* shall meet the requirements of EN ISO 3696 - quality 3
- *Isopropyl alcohol*, anhydrous (less than 0,9 % (V/V) water)
- *Toluene*
- *Titration solvent*: prepared by mixing toluene, anhydrous isopropyl alcohol and water in the ratio 50/49.5/0.5. The titration solvent should be made up in large quantities, and its blank value determined daily by titration prior to use.
- *Potassium hydroxide solution*, standard alcoholic (0,1 mol/L). Use commercial product or prepare the product (see below). Standardize frequently potassium hydroxide solution to detect changes of 0,0005 N. One way to do this is as follows: weigh, to the nearest 0,1mg approximately 0,2 g of potassium acid phtalate and dissolve in (40 ± 1) mL of water, free of CO_2. Add six drops of phenolphtalein; titrate with the potassium hydroxide alcoholic. Perform a blank titration on the water used to dissolve the potassium acid phtalate.

Calculate the normality using the following formula:

$$\text{Normality} = (W_p/204{,}23)*(1000/(V-V_b))$$

where:

W_p corresponds to the mass of potassium acid phthalate in g.

V corresponds to the volume of titrant used to titrate the salt to the specific end point in ml.

V_b corresponds to the volume of titrant used to titrate the blank in ml.

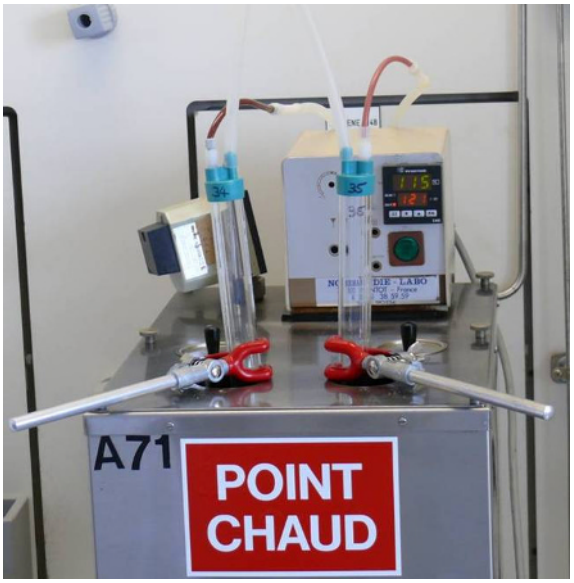
Add 6 g of solid KOH to approximately 1 l of anhydrous isopropyl alcohol (containing less than 0,9 % water) in a 2 l Erlenmeyer flask. Boil the mixture gently for 10 min to 15 min, while stirring to prevent the solids from forming a cake at the bottom. Add at least 2 g of barium hydroxide ($Ba(OH)_2$) and again boil gently for 5 min to 10 min. Cool to room temperature, allow to stand for several hours, and filter the supernatant liquid through a fine sintered-glass or porcelain filtering funnel; avoid unnecessary exposure to carbon dioxide (CO_2) during filtration. Store the solution in a chemically resistant dispensing bottle out of contact with cork, rubber, or saponifiable stopcocks lubricant and protected by a guard tube containing soda lime or soda non-fibrous silicate absorbent.

7 Procedure

7.1 Ageing of the sample

- Note the weight of the empty tube (1) with the O_2-delivery tube (2).
- Weigh (10 ± 0,2) g of the fuel in the glass tube (1).
- Set up the oxidation cell : assemble cap (3) and O_2-delivery tube (2) onto the tube, then part 4 and 5. Plug main O_2-delivery tube (6) and exhaust tube (7).
- Open the oxygen valve and adjust oxygen rate at (1 ± 0,1) l/h.
- Check that oxygen is bubbling in the oxidation cells.
- Plunge the test cells in the heating bath when the oil temperature is stabilized at (115 ± 0,2) °C (30 min to 1 h after having switched on the apparatus).

NOTE It is essential that the level of the fuel in the oxidation cells be 2 cm below the level of the oil in the heating bath in order to ensure a homogeneous oxidation temperature. It is easier to mark the level on the flask before immersion in the bath.

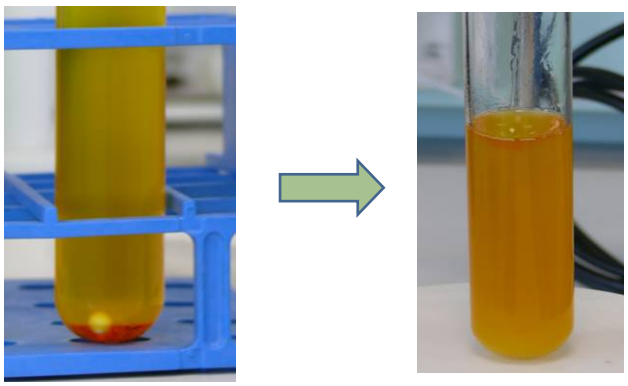


Positioning cells in the bath

- Let oxidation occur during 16 h ± 5 min.
- Remove oxidation cells from the bath and check that oxygen is still bubbling in the cells.
- Disconnect oxygen.
- Clean carefully (with petroleum ether and acetone) the external part of the oxidation cell to remove oil.
- Plunge the sealed sample into a bath containing water and ice bath for 10min to stop the oxidation process.
- Place the sealed sample at room temperature (20 to 25) °C in the dark at least 1 h.
- Determine the sample aspect through visual inspection (clear and bright, hazy, two phases, etc.).

7.2 Measurement of acid number

- Remove parts (3) to (7).
- Weigh the oxidation cell (1) with the O_2-delivery tube (2) to calculate the mass of aged product (W).
- Add 10 mL of the titration solvent directly in the test cell (by the O_2-delivery tube to rinse it) then remove the O_2-delivery tube.
- Stir vigorously (magnetic stirrer) the aged sample until a homogeneous mixture is achieved:



- Pour the mixture into a 250 mL beaker or a suitable titration vessel and rinse the oxidation cell with 5 mL solvent.
- Add 85 mL of solvent and without delay run the titration at a temperature between 15 °C and 25 °C.

Automatic titration method:

- Prepare the electrodes as directed in 8.2 of ASTM D664.
- Place the beaker on the titration stands and adjust its position so that the electrodes are about half immersed.
- Start the stirrer and stir throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution.
- Select the right burette, fill with the 0,1 M alcoholic KOH solution and place the burette in position on the titration assembly, ensuring that the tip is immersed about 25 mm in titration vessel liquid.
- Adjust the apparatus in accordance with the manufacturer's instructions to provide a dynamic mode of titrant addition: the apparatus shall be programmed such that when an inflection point is approached, the rate of addition and volume of titrant added are based on the change in slope of the titration curve.
- Suggested parameters:
  - Blank parameters
    - min increment volume = 10 µL
  - Titration parameters:
    - min increment volume = 10 µL
    - measuring point density = 4 (at least for Metrohm apparatus)
    - signal drift = 50 mV/min
  - Addition of p-naphtolbenzein (few drops) as check indicator: this is only a visual checking to "validate" the equivalence point determined by the potentiometric titration. This equivalence point has to correspond to the color change from orange to green or green-brown.
- An equivalence point is recognizable if the first derivative of the titration curve produces a maximum, which is significantly higher than the noise produced by electrostatic effects.

- Note the amount of KOH necessary to reach the end point (A).
- Remove the titration solution, rinses the electrodes and burette tip with the titration solvent, then with isopropyl alcohol and finally with reagent grade water. Immerse the electrodes in water for at least 5min before starting another titration to restore the aqueous gel layer of the glass electrode. After 5 min in the water, rinse the electrodes with isopropyl alcohol then the titration solvent before proceeding to the next titration.

Blank titration:

Just before starting the analysis sequence, perform a blank titration on 100 mL of the titration solvent (with few drops of p-naphtolbenzein) and 0,1 M KOH solution according to the previous dynamic mode of titrant addition. Note the amount of KOH necessary to reach the end point (B), corresponding to the color change from orange to green or green-brown.

8 Calculation

Calculate the acid number by using the following formula:

Acid number, mg of KOH/g = [(A-B)M x 56,1] / W

where:

A corresponds to the volume of KOH solution required for titration of the sample, mL

B corresponds to the volume of KOH solution required for titration of the blank, mL

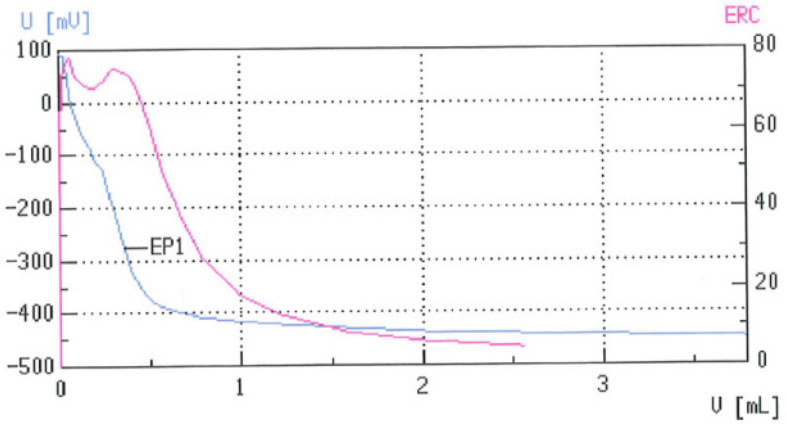
M corresponds to the molarity of the KOH solution

W corresponds to the mass of sample, g.

9 Recommendations on titration curve

Derivative curve with a double-peak without returning to baseline:

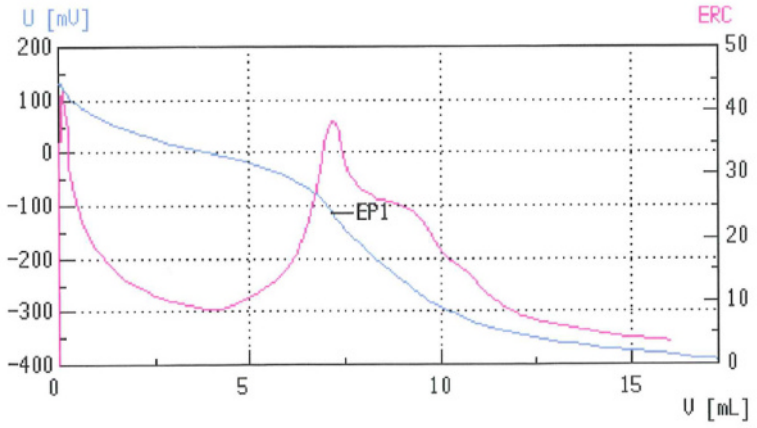
A good reading of the equivalent point is made by the use of the derivative of the titration curve. The total acidity is defined on the whole peak (curve in blue and derivative curve in pink) as shown in the following graph.



Equivalent point (EP1) from a curve with a double-peak

Derivative curve with two separate peaks:

In any case the reading has to be made based on the extremum defined by the derivative (see the graph below). The use of the colored indicator allows validating the extremum detected automatically by the titration software and that has to coincide with the change of color of the colored indicator. This practice eliminates any questioning on the attribution of the right EP1 by the software.



Equivalent point (EP1) from a curve with two peaks

Derivative curve with two separate peaks: check of the potential from the electrode.

It is strongly recommended to measure the standard solution at pH11 in addition to pH4 and pH7. Indeed, this standard solution gives an idea of the potential observed for a basic solution. The potential of Nernst at pH7 is U=0,059V (equilibrium potential given by the electrode with regard to the standard potential of the RedOx system involved). For any acid solution the potential is > 59 mV; for any basic solution it is < 59 mV.

10 Result report

Report the acid number of the aged sample in mg KOH/g rounded to the nearest 0,01.

Appendix Cleaning procedure for oxidation cells

The use of new glass tubes (1) and oxygen delivery tubes (2) is recommended in order to save the cleaning procedure.

Always wash the plastic parts (tube caps (3), connectors (5), etc.) with 2-propanol in order to remove organic residues. Rinse with tap water and finally with demineralised or distilled water. Dry them in an oven for at least 2 h at 80 °C.

If not replaced, wash the glass tubes (1) and the oxygen delivery tube (2) at least three times with trisolvent mixture[3] in order to remove residual fuel and adherent ageing organic residues. The last solvent portion should be colourless. Rinse with 2-Propanol and tap water. Put the delivery tube into the glass tube and fill completely with an aqueous alkaline laboratory cleaning solution. Store the glass tubes and the oxygen delivery tubes at room temperature over night. Rinse the glass tubes and the oxygen delivery tubes thoroughly with tap water and finally with demineralised or distilled water. Dry them in an oven for at least 2 h at 110 °C.

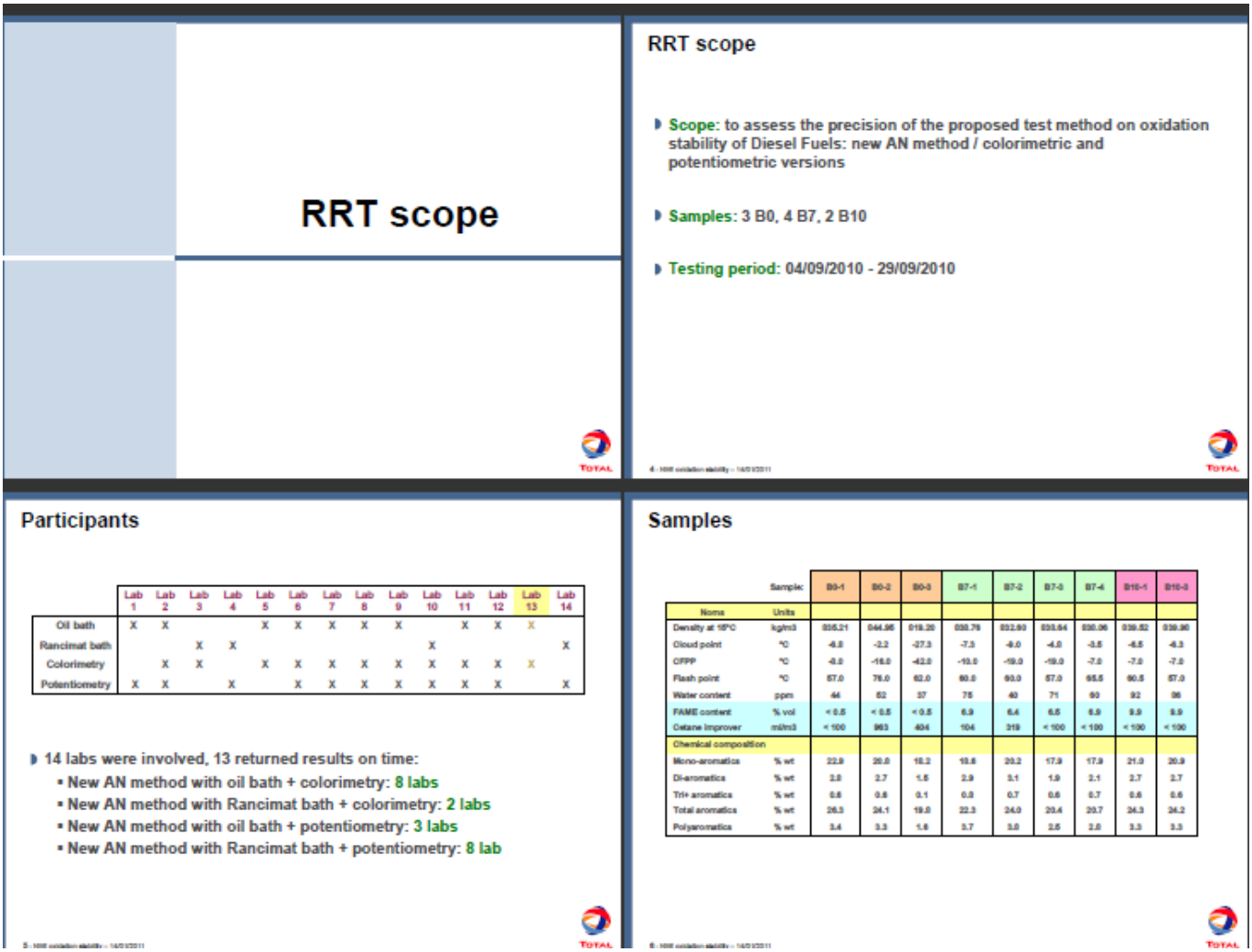
[3] Trisolvent mixture, consisting of methanol/toluene/acetone 1:1:1 (by volume).

Annex B
(normative)

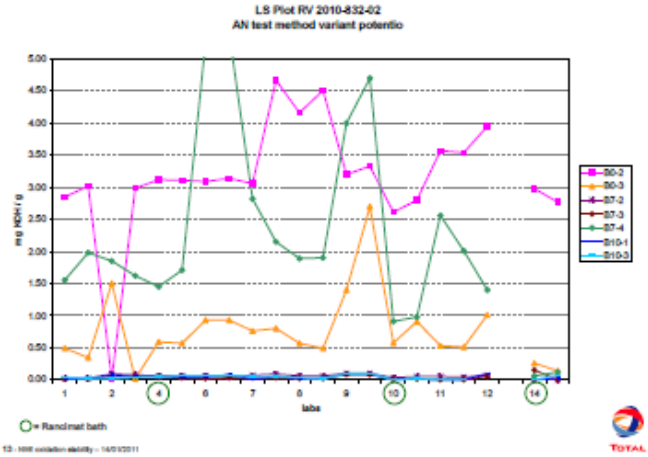
Round Robin Results

B.1 October 2010 results

The first assessment results are given below.

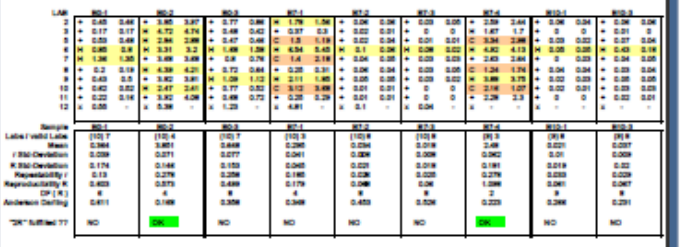


Potentiometry

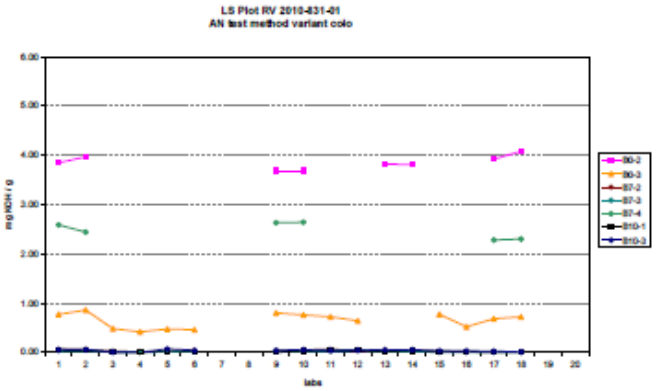


Stat. treatment (EN ISO 4259)

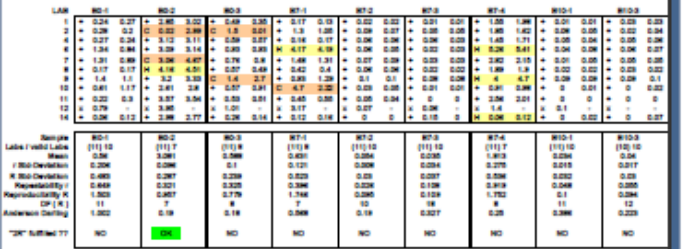
Colorimetry



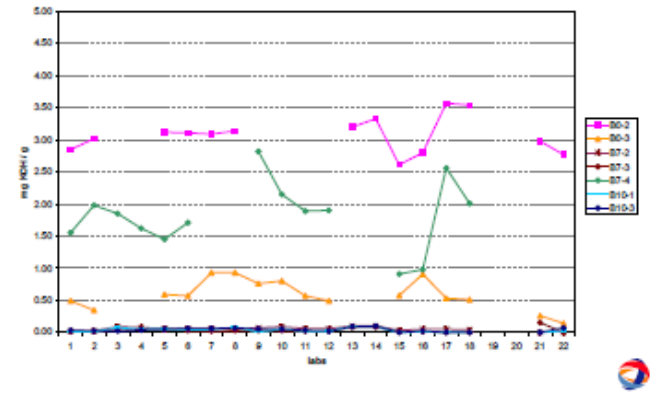
Colorimetry



Potentiometry



Potentiometry



B.2 2012/2013 RRT

Seven laboratories provided full sets of results, meaning results on both Part 1 and Part 2. The statistical processing has been done on those seven full sets of data.

Statistical evaluation of the results was performed by the CEN/TC 19/WG 36 according to the methodology indicated in EN ISO 4259 [4]. Both linear and logarithmic models were used to evaluate the repeatability and reproducibility. Results are given in Figure B.1 and Table B.1 for linear treatment and in Figure B.2 and Table B.2 for log treatment. For each sample, the following data are detailed:

1) the number of participating / valid labs,

2) the mean value,

3) the repeatability (r) and reproducibility (R) including the degrees of freedom (for R only),

4) the Anderson Darling Criterium ("AD"), which can be used as a quick numeric indicator for the quality of the normal distribution (values below 1 are usually considered as satisfactory),

5) the fulfilment of the "2R" rule: is 2R<mean ?

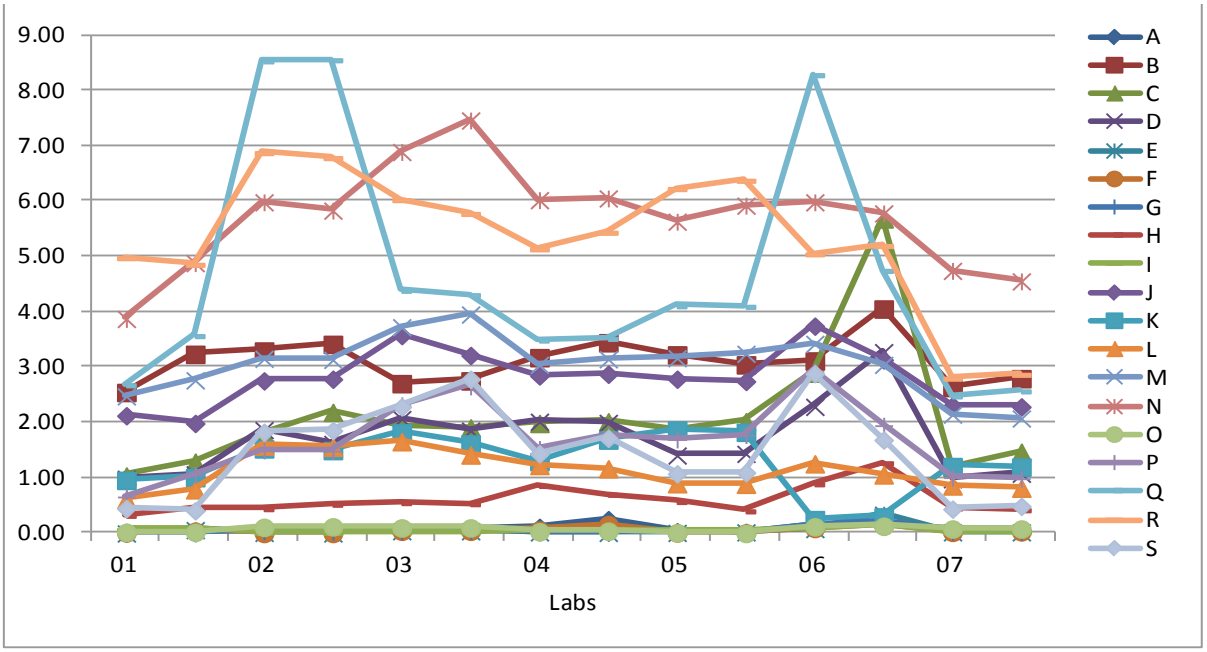


Figure B.1 — AN values measured by the participants on the 19 samples

Table B.1 — EN ISO 4259 statistical processing of the data by applying the linear model

LAB/SAMPLE	A		B		C		D		E		F		G		H		I	
1	+ 0.02	0.02	+ 2.55	3.24	+ 1.04	1.29	+ 0.99	1.07	+ 0	0.06	+ 0.01	0.04	+ 0	0	+ 0.32	0.45	+ 0.06	0.07
2	+ 0.04	0.05	+ 3.3	3.42	+ 1.79	2.19	+ 1.87	1.62	+ 0.01	0	+ 0	0	+ 0.04	0.03	+ 0.44	0.52	+ 0.01	0.01
3	+ 0.07	0.08	+ 2.71	2.76	+ 1.92	1.91	+ 2.07	1.86	+ 0.04	0.04	+ 0.04	0.04	+ 0.04	0.05	+ 0.55	0.53	+ 0.02	0.02
4	+ 0.11	0.25	+ 3.18	3.45	+ 1.99	2.02	+ 2.02	2	+ 0.02	0.01	+ 0.06	0.16	+ 0.02	0.02	+ 0.86	0.7	+ 0.03	0.04
5	+ 0.03	0.02	+ 3.23	3.05	+ 1.86	2.02	+ 1.41	1.44	+ 0.01	0.02	+ 0.01	0.01	+ 0.03	0.02	+ 0.57	0.4	+ 0.04	0.03
6	+ 0.15	0.15	+ 3.12	4.06	C 2.9	5.69	+ 2.29	3.28	+ 0.08	0.34	+ 0.09	0.14	+ 0.16	0.22	+ 0.89	1.27	+ 0.07	0.13
7	+ 0.07	0.06	+ 2.64	2.8	+ 1.2	1.47	+ 0.98	1.08	+ 0.02	0.02	+ 0.02	0.03	+ 0.03	0.03	+ 0.45	0.42	+ 0.02	0.02
SAMPLE	A		B		C		D		E		F		G		H		I	
Labs / Valid Labs	(7) 7		(7) 7		(7) 6		(7) 7		(7) 7		(7) 7		(7) 7		(7) 7		(7) 7	
Mean	0.08		3.10786		1.725		1.71286		0.04786		0.04643		0.04929		0.59786		0.04071	
Repeatability r	0.126		1.095		0.568		0.937		0.239		0.104		0.056		0.422		0.056	
Reproducibility R	0.220		1.269		1.354		2.178		0.275		0.165		0.224		0.860		0.110	
Reproducibility %R	275.4		40.8		78.5		127.1		573.9		356.3		454.7		143.8		270.3	
DF	8		11		6		7		11		9		6		8		8	
Anderson Darling	0.43		0.27		0.75		0.27		1.35		0.62		1.13		0.65		0.49	
Factor R/r	1.75		1.16		2.39		2.32		1.15		1.60		4.02		2.04		1.98	
OK Yes/No	No		Yes		No		No		No		No		No		No		No	

LAB/SAMPLE	J		K		L		M		N		O		P		Q		R		S	
1	+ 2.13	1.99	+ 0.96	1.01	+ 0.61	0.79	+ 2.48	2.77	+ 3.88	4.89	+ 0.02	0.02	+ 0.66	1.06	+ 2.68	3.57	+ 4.98	4.86	+ 0.45	0.41
2	+ 2.76	2.79	+ 1.53	1.5	+ 1.58	1.56	+ 3.16	3.14	+ 5.99	5.84	+ 0.11	0.12	+ 1.5	1.49	H 8.54	8.56	+ 6.88	6.79	+ 1.83	1.86
3	+ 3.58	3.22	+ 1.82	1.62	+ 1.66	1.42	+ 3.73	3.96	H 6.9	7.47	+ 0.1	0.1	+ 2.32	2.66	+ 4.39	4.31	+ 6.03	5.78	+ 2.29	2.79
4	+ 2.85	2.88	+ 1.3	1.69	+ 1.23	1.17	+ 3.05	3.15	+ 6.03	6.06	+ 0.03	0.04	+ 1.53	1.77	+ 3.49	3.52	+ 5.14	5.44	+ 1.44	1.72
5	+ 2.79	2.75	+ 1.87	1.83	+ 0.9	0.89	+ 3.17	3.25	+ 5.64	5.93	+ 0.01	0	+ 1.7	1.78	+ 4.11	4.1	+ 6.23	6.38	+ 1.08	1.1
6	+ 3.75	3.14	+ 0.25	0.3	+ 1.26	1.06	+ 3.43	3.05	+ 5.99	5.79	+ 0.12	0.13	+ 2.93	1.95	C 8.29	4.75	+ 5.05	5.2	C 2.89	1.69
7	+ 2.31	2.29	+ 1.21	1.2	+ 0.86	0.82	+ 2.15	2.08	+ 4.75	4.56	+ 0.08	0.08	+ 1.01	0.99	+ 2.48	2.57	H 2.8	2.87	+ 0.44	0.49
SAMPLE	J		K		L		M		N		O		P		Q		R		S	
Labs / Valid Labs	(7) 7		(7) 7		(7) 7		(7) 7		(7) 6		(7) 7		(7) 7		(7) 5		(7) 6		(7) 6	
Mean	2.80214		1.29214		1.12929		3.04071		5.44583		0.06857		1.66786		3.522		5.73		1.325	
Repeatability r	0.646		0.399		0.329		0.491		1.097		0.018		1.017		1.033		0.469		0.578	
Reproducibility R	1.772		1.879		1.157		1.911		2.636		0.168		2.233		2.779		2.741		3.031	
Reproducibility %R	63.2		145.4		102.4		62.9		48.4		244.7		133.9		78.9		47.8		228.7	
DF	7		6		7		6		6		6		7		5		5		5	
Anderson Darling	0.29		0.35		0.29		0.38		0.71		0.32		0.29		0.18		0.25		0.23	
Factor R/r	2.74		4.71		3.52		3.89		2.40		9.41		2.19		2.69		5.84		5.24	
OK Yes/No	No		No		No		No		Yes		No		No		No		Yes		No	

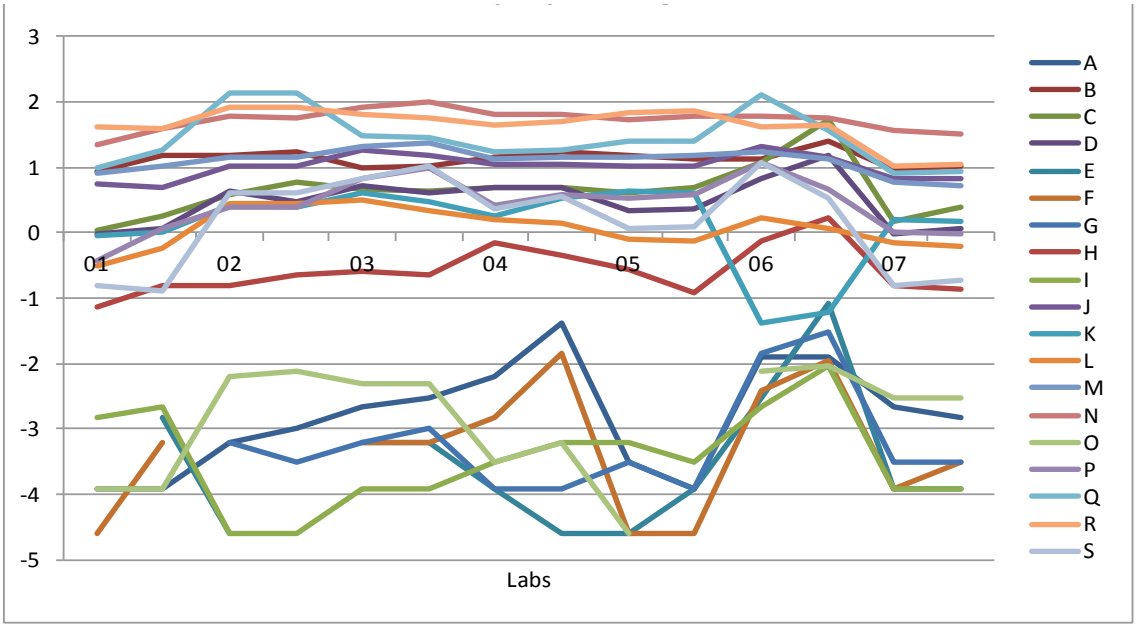


Figure B.2 — log(AN) calculated from AN values measured by the participants on the 19 samples

Table B.2 — EN ISO 4259 statistical processing of the data by applying the logarithmic model

LAB/SAMPLE	A		B		C		D		E		F		G		H		I	
1	+ -3.912	-3.9	+ 0.936	1.18	+ 0.039	0.26	+ -0.01	0.07	x -	-2.8	C -4.605	-3.2	x -	-	+ -1.139	-0.8	+ -2.813	-2.7
2	+ -3.219	-3	+ 1.194	1.23	+ 0.582	0.78	+ 0.626	0.48	x -4.605	-	x -	-	+ -3.219	-3.5	+ -0.821	-0.7	+ -4.605	-4.6
3	+ -2.659	-2.5	+ 0.997	1.02	+ 0.652	0.65	+ 0.728	0.62	+ -3.219	-3.2	+ -3.219	-3.2	+ -3.219	-3	+ -0.598	-0.6	+ -3.912	-3.9
4	+ -2.207	-1.4	+ 1.157	1.24	+ 0.688	0.7	+ 0.703	0.69	+ -3.912	-4.6	+ -2.813	-1.8	+ -3.912	-3.9	+ -0.151	-0.4	+ -3.507	-3.2
5	+ -3.507	-3.9	+ 1.172	1.12	+ 0.621	0.7	+ 0.344	0.37	+ -4.605	-3.9	+ -4.605	-4.6	+ -3.507	-3.9	+ -0.562	-0.9	+ -3.219	-3.5
6	+ -1.897	-1.9	+ 1.138	1.4	+ 1.065	1.74	+ 0.829	1.19	C -2.526	-1.1	+ -2.408	-2	H -1.833	-1.5	+ -0.117	0.24	+ -2.659	-2
7	+ -2.659	-2.8	+ 0.971	1.03	+ 0.182	0.39	+ -0.02	0.08	+ -3.912	-3.9	+ -3.912	-3.5	+ -3.507	-3.5	+ -0.799	-0.9	+ -3.912	-3.9
SAMPLE	A		B		C		D		E		F		G		H		I	
Labs / Valid Labs	(7) 7		(7) 7		(7) 7		(7) 7		(7) 4		(6) 5		(6) 5		(7) 7		(7) 7	
Mean	-2.8216		1.12643		0.64607		0.47814		-3.912		-3.2087		-3.5198		-0.5841		-3.4629	
Repeatability r	0.860		0.336		0.685		0.375		1.362		1.320		0.626		0.594		0.675	
Reproducibility R	2.800		0.399		1.388		1.242		2.154		3.765		1.211		1.278		2.691	
Reproducibility %R	99.245		35.446		214.771		259.786		55.060		117.344		34.398		218.743		77.701	
DF	7.0		11.0		8.0		7.0		4.0		5.0		5.0		7.0		6.0	
Anderson Darling	0.228		0.306		0.545		0.275		0.415		0.232		0.137		0.435		0.21	
Factor R/r	3.26		1.19		2.03		3.31		1.58		2.85		1.93		2.15		3.99	
OK (Yes/No)	No		Yes		No		No		No		No		Yes		No		No	

LAB/SAMPLE	J		K		L		M		N		O		P		Q		R		S	
1	+ 0.756	0.69	+ -0.041	0.01	+ -0.494	-0.2	+ 0.908	1.02	+ 1.356	1.59	+ -3.912	-3.9	+ -0.416	0.06	+ 0.986	1.27	+ 1.605	1.58	+ -0.799	-0.9
2	+ 1.015	1.03	+ 0.425	0.41	+ 0.457	0.45	+ 1.151	1.14	+ 1.79	1.77	+ -2.207	-2.1	+ 0.405	0.4	+ 2.145	2.15	+ 1.929	1.92	+ 0.604	0.62
3	+ 1.275	1.17	+ 0.599	0.48	+ 0.507	0.35	+ 1.316	1.38	+ 1.932	2.01	+ -2.303	-2.3	+ 0.842	0.98	+ 1.479	1.46	+ 1.797	1.75	+ 0.829	1.03
4	+ 1.047	1.06	+ 0.262	0.53	+ 0.207	0.16	+ 1.115	1.15	+ 1.797	1.8	+ -3.507	-3.2	+ 0.425	0.57	+ 1.25	1.26	+ 1.637	1.69	+ 0.365	0.54
5	+ 1.026	1.01	+ 0.626	0.6	+ -0.105	-0.1	+ 1.154	1.18	+ 1.73	1.78	x -4.605	-	+ 0.531	0.58	+ 1.413	1.41	+ 1.829	1.85	+ 0.077	0.1
6	+ 1.322	1.14	+ -1.386	-1.2	+ 0.231	0.06	+ 1.233	1.12	+ 1.79	1.76	+ -2.12	-2	+ 1.075	0.67	+ 2.115	1.56	+ 1.619	1.65	+ 1.061	0.53
7	+ 0.837	0.83	+ 0.191	0.18	+ -0.151	-0.2	+ 0.765	0.73	+ 1.558	1.52	+ -2.526	-2.5	+ 0.01	-0	+ 0.908	0.94	+ 1.03	1.05	+ -0.821	-0.7
SAMPLE	J		K		L		M		N		O		P		Q		R		S	
Labs / Valid Labs	(7) 7		(7) 7		(7) 7		(7) 7		(7) 7		(7) 6		(7) 7		(7) 7		(7) 7		(7) 7	
Mean	1.01457		0.12		0.07943		1.09671		1.7265		-2.7246		0.43664		1.45343		1.639		0.18	
Repeatability r	0.196		0.308		0.316		0.161		0.228		0.311		0.587		0.560		0.079		0.549	
Reproducibility R	0.641		2.296		1.056		0.668		0.587		2.713		1.425		1.452		1.001		2.544	
Reproducibility %R	63.148		1913.183		1329.019		60.870		34.012		99.561		326.434		99.908		61.054		1413.361	
DF	7.0		6.0		7.0		6.0		7.0		5.0		7.0		7.0		6.0		6.0	
Anderson Darling	0.306		0.83		0.244		0.457		0.45		0.465		0.271		0.21		0.572		0.444	
Factor R/r	3.28		7.44		3.34		4.14		2.57		8.71		2.43		2.59		12.60		4.64	
OK (Yes/No)	No		No		No		No		Yes		No		No		No		No		No	

Annex C
(normative)

Pass-/Fail discriminant analysis

The results of the preliminary test were examined by the experts during the 5th meeting that took place at IFP Energies Nouvelles the 2nd of September 2011.

Based on AN and aspect results, the experts were in charge of evaluating each sample in order to find a consensus on their classification as Pass sample or Fail sample. The experts have decided to take into account the AN value as main criterion; the aspect parameter was used to help the classification for samples with "intermediate" AN values, which means samples that do not have very low or very high AN value.

Thanks to this reasoning and after some discussion on few samples, a consensus was reached with the group and the samples are now classified as reported in Table C.1 to Table C.3.

NOTE One CEN expert raised the problems that will occur on some specific samples. Indeed, samples supplied by Neste Oil such as MK1 and Finnish winter grade diesel (fulfilling EN 590 [5] criteria) even without FAME do not pass this test, if the pass or fail classification is determined from the AN values. Nevertheless, these fuels have been used since 1990, and there has not been any problem with long term storage or oxidation stability. Cars have been running well with these fuels.

As we do not have information on the behaviour in service of all samples, it has been decided to not take this parameter into account for the description of the Bx. Nevertheless, it will be important to keep in mind the remark in the NOTE above regarding works to come, especially for the definition of the scope of the new AN method.

Table C.1 — Preliminary test results and Pass/Fail classification of B0 samples

Bx	Sample code	Date of test	AN after ageing (mg KOH/g)	Sample aspect after ageing	Pass/Fail classif
B0	AK	10/08/2011	0.16	Clear	Pass
	BA	23/08/2011	0.19	Cloudy	Pass
	AT	17/08/2011	0.15	Clear	Pass
	AR	10/08/2011	0.24	Clear	Pass
	AD	10/08/2011	0.09	Clear	Pass
	BI	10/08/2011	1.09	Clear	Fail
	BM	25/08/2011	1.07	Cloudy	Fail
	AW	23/08/2011	2.94	Cloudy	Fail
	AM	23/08/2011	1.47	Cloudy	Fail
	AU	23/08/2011	0.26	Cloudy	Pass
	AB	23/08/2011	3.27	Cloudy	Fail
	AN	25/08/2011	3.39	Cloudy	Fail
	AP	23/08/2011	2.68	Cloudy	Fail
	BB	24/08/2011	2.15	Cloudy	Fail

Table C.2 — Preliminary test results and Pass/Fail classification of B5 and B7 samples

Bx	Sample code	Date of test	AN after ageing (mg KOH/g)	Sample aspect after ageing	Pass/Fail classif
B5	BQ	24/08/2011	8.02	Cloudy	Fail
	AO	24/08/2011	9.01	Cloudy	Fail
B7	AX	25/08/2011	0.41	Clear	Pass
	BG	11/08/2011	3.3	Cloudy	Fail
	BN	11/08/2011	0.22	Clear	Pass
	AF	17/08/2011	0.17	Clear	Pass
	AZ	17/08/2011	0.20	Clear	Pass
	AY	17/08/2011	0.21	Clear	Pass
	AG	17/08/2011	3.28	Cloudy	Fail
	AC	24/08/2011	0.57	Cloudy	Fail
	AA	17/08/2011	0.21	Clear	Pass
	BJ	24/08/2011	1.03	Cloudy	Fail
	BP	11/08/2011	0.87	Cloudy	Fail
	AS	25/08/2011	6.04	Cloudy	Fail
	BR	24/08/2011	8.52	Cloudy	Fail
	BH	11/08/2011	8.21	Cloudy	Fail

Table C.3 — Preliminary test results and Pass/Fail classification of B8 and B10 samples

Bx	Sample code	Date of test	AN after ageing (mg KOH/g)	Sample aspect after ageing	Pass/Fail classif
B8	AH	25/08/2011	6.26	Cloudy	Fail
B10	BF	12/08/2011	0.23	Clear	Pass
	BK	11/08/2011	0.53	Clear	Pass
	AJ	12/08/2011	0.22	Clear	Pass
	BD	12/08/2011	0.31	Clear	Pass
	BC	18/08/2011	0.66	Cloudy	Fail
	AI	12/08/2011	0.23	Clear	Pass
	BE	18/08/2011	0.34	Clear	Pass
	BO	18/08/2011	0.36	Clear	Pass
	AL	12/08/2011	0.44	Clear	Pass
	AQ	18/08/2011	7.69	Cloudy	Fail
	AV	12/08/2011	2.48	Cloudy	Fail
	AE	18/08/2011	5.59	Cloudy	Fail
	BL	18/08/2011	10.31	Cloudy	Fail

The assessment is presented below.

- **B0 to B10**
- supplied by PSA, Neste Oil, OMV, TOTAL
- Bx directly supplied as Bx or prepared by mixing B0 and FAME
- No mixing between « good » and « bad » Bx, thanks to the previous RRT results

→ 14*B0 2*B5 14*B7 1*B8 13*B10

- **Measurement of AN and sample aspect (clear or cloudy) after ageing, on each sample, by one lab (TOTAL/CReG)** – from the 2011/08/10 to the 2011/08/25
- **AN from 0.09 mgKOH/g to 10.31 mgKOH/g**

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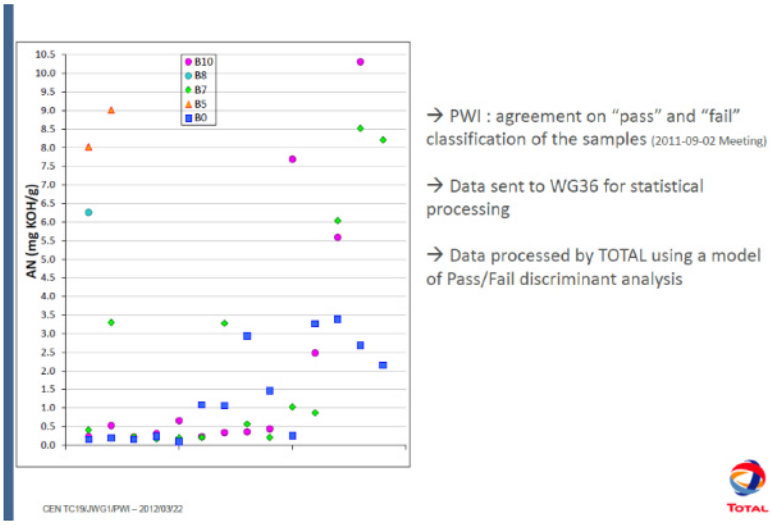
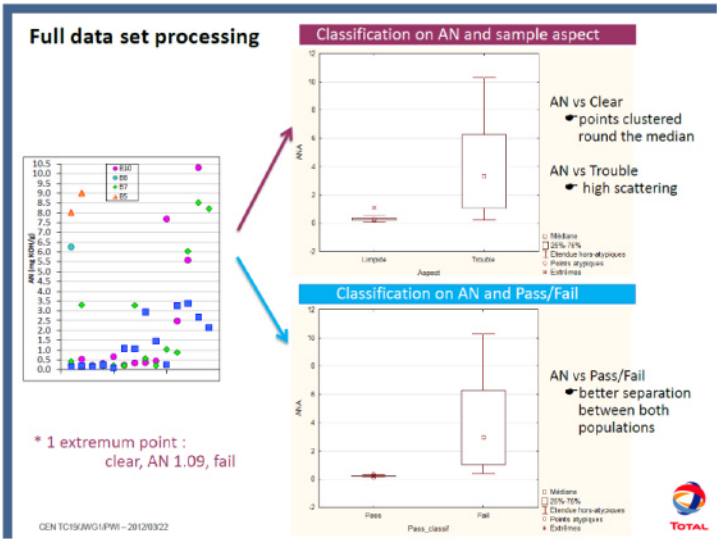
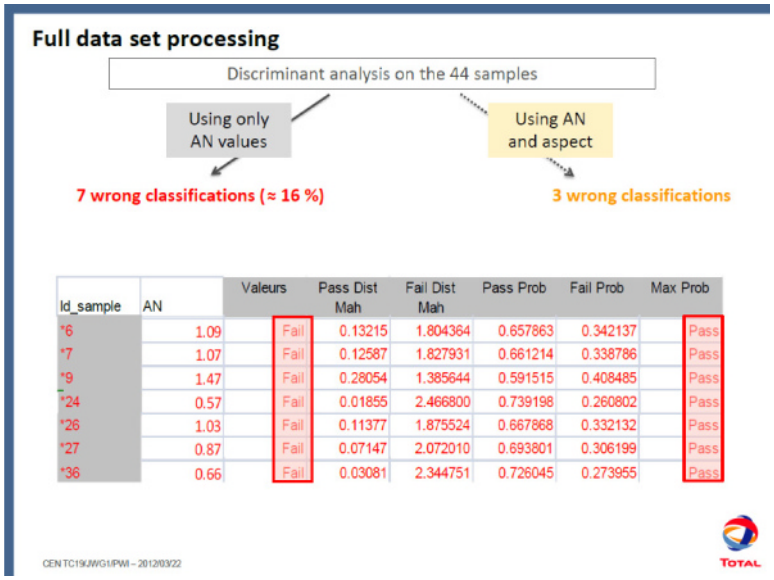
TOTAL





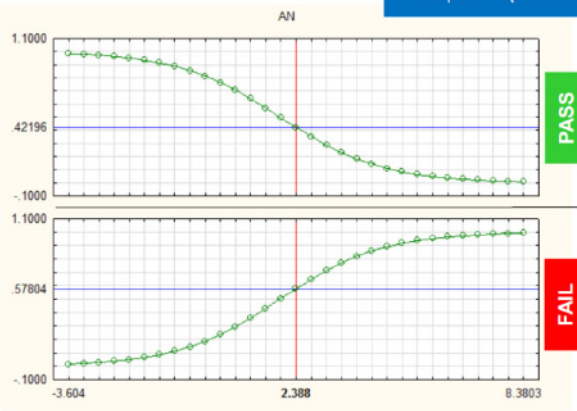


Id_sample	AN	Valeurs	Pass Dist Mah	Fail Dist Mah	Pass Prob	Fail Prob	Max Prob
*6	1.09	Fail	0.13215	1.804364	0.657863	0.342137	Pass
*7	1.07	Fail	0.12587	1.827931	0.661214	0.338786	Pass
*9	1.47	Fail	0.28054	1.385644	0.591515	0.408485	Pass
*24	0.57	Fail	0.01855	2.466800	0.739198	0.260802	Pass
*26	1.03	Fail	0.11377	1.875524	0.667868	0.332132	Pass
*27	0.87	Fail	0.07147	2.072010	0.693801	0.306199	Pass
*36	0.66	Fail	0.03081	2.344751	0.726045	0.273955	Pass

Full data set processing

Pass prob = (-0.794843) + 0.049408*AN

Fail prob = (-2.26198) + 0.79560*AN



→ Highest probability based on the matrix of data : **40 % of confidence to be Pass**

TOTAL

Classification using 1.0 threshold AN

- each sample with AN > 1.0 mgKOH/g automatically Fail

- take off of the samples with AN > 1.0 mgKOH/g

→ matrix of 23 samples
→ Pass population larger than Fail population

→ **0 wrong classification**

→ 1.0 threshold AN classification function :

Pass prob = (-2.71878) + 19.95369*AN

Fail prob = (-20.9485) + 54.0332*AN

TOTAL

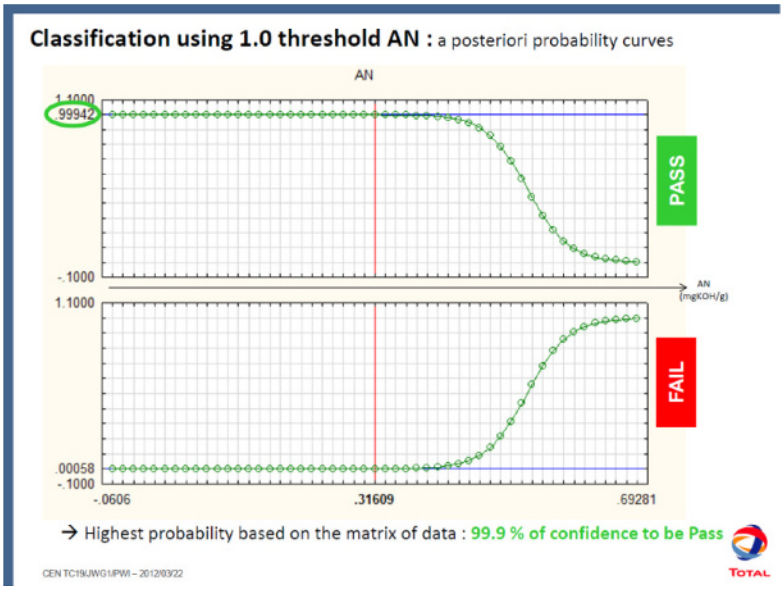
Classification using 1.0 threshold AN : matrix of 23 samples

Statistiques pour Chaque Obs. (Threshold1 dans CEN TC19 JWG1 PWI_2011_AN method_Preliminary test_a)
Les classifications incorrectes sont marquées par *
Echantillon d'analyse N = 23

N° d'observ.	Valeurs Classif.	Pass Dis. Mah	Fail Dis. Mah	PASS	FAIL	Prob. + forte	Seconde Prob.
1	Pass	2.19161	28.72250	1.000000	0.000000	Pass	Fail
2	Pass	0.90870	23.35006	0.999998	0.000002	Pass	Fail
3	Pass	0.74892	22.50868	0.999997	0.000003	Pass	Fail
4	Pass	0.60457	21.68275	0.999996	0.000004	Pass	Fail
5	Pass	0.36220	20.07719	0.999992	0.000008	Pass	Fail
6	Pass	0.26416	19.29757	0.999989	0.000011	Pass	Fail
7	Pass	0.18157	18.53338	0.999984	0.000016	Pass	Fail
8	Pass	0.18157	18.53338	0.999984	0.000016	Pass	Fail
9	Pass	0.11442	17.78464	0.999978	0.000022	Pass	Fail
10	Pass	0.11442	17.78464	0.999978	0.000022	Pass	Fail
11	Pass	0.06270	17.05133	0.999969	0.000031	Pass	Fail
12	Pass	0.06270	17.05133	0.999969	0.000031	Pass	Fail
13	Pass	0.02642	16.33346	0.999957	0.000043	Pass	Fail
14	Pass	0.00017	14.94404	0.999915	0.000085	Pass	Fail
15	Pass	0.20473	11.74064	0.999531	0.000469	Pass	Fail
16	Pass	0.51272	10.00386	0.998698	0.001302	Pass	Fail
17	Pass	0.79523	8.92320	0.997430	0.002570	Pass	Fail
18	Pass	1.77169	6.49170	0.986035	0.013965	Pass	Fail
19	Pass	2.54282	5.21806	0.962121	0.037879	Pass	Fail
20	Pass	5.68987	2.23080	0.541798	0.458202	Pass	Fail
21	Fail	7.48995	1.30452	0.232260	0.767740	Fail	Pass
22	Fail	12.44325	0.12350	0.013888	0.986112	Fail	Pass
23	Fail	28.86393	2.23080	0.000011	0.999989	Fail	Pass

→ **0 wrong classification**

TOTAL


Classification using 1.0 threshold AN : a posteriori probability curves
AN
1.1000
.99942
-.1000
PASS
AN (mgKOH/g)
1.1000
.00058
-.1000
FAIL
-.0606
.31609
.69281
→ Highest probability based on the matrix of data : 99.9 % of confidence to be Pass
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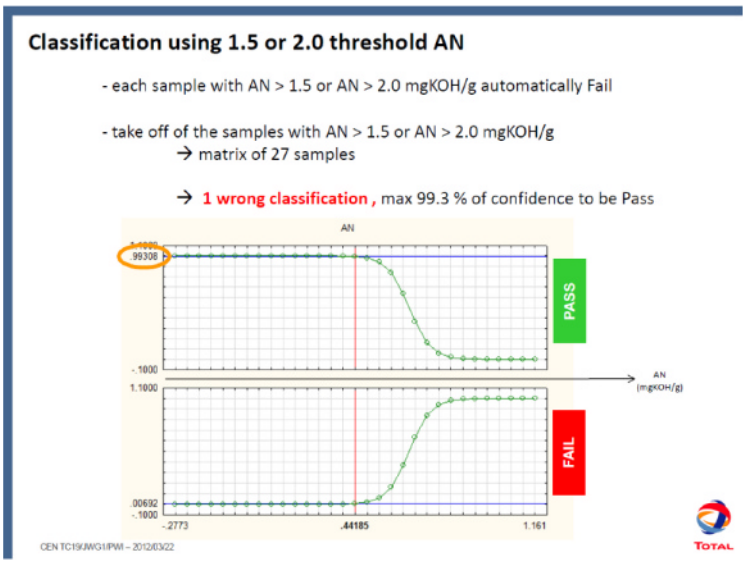
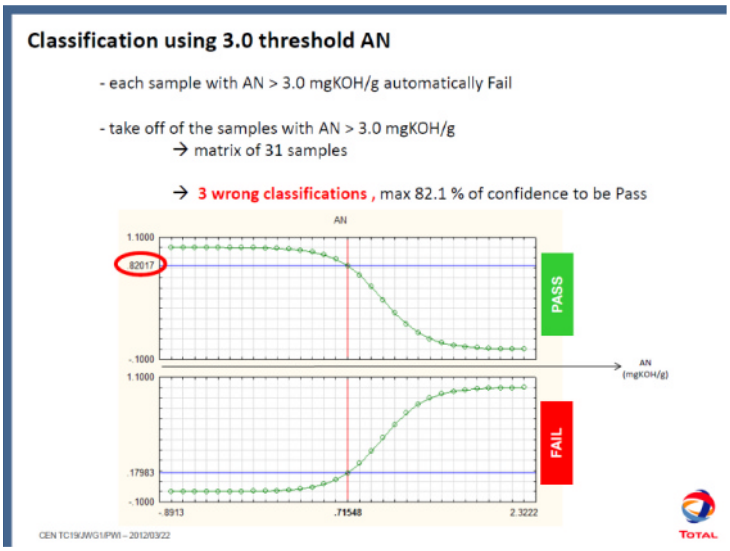
TOTAL


Classification using 1.5 or 2.0 threshold AN
- each sample with AN > 1.5 or AN > 2.0 mgKOH/g automatically Fail
- take off of the samples with AN > 1.5 or AN > 2.0 mgKOH/g
→ matrix of 27 samples
→ 1 wrong classification , max 99.3 % of confidence to be Pass
AN
99308
-.1000
PASS
AN (mgKOH/g)
1.1000
.00692
-.1000
FAIL
-.2773
.44185
1.161
CEN TC19/JWG1/PWI – 2012/03/22
TOTAL


Classification using 3.0 threshold AN
- each sample with AN > 3.0 mgKOH/g automatically Fail
- take off of the samples with AN > 3.0 mgKOH/g
→ matrix of 31 samples
→ 3 wrong classifications , max 82.1 % of confidence to be Pass
AN
1.1000
.82017
-.1000
PASS
AN (mgKOH/g)
1.1000
.17983
-.1000
FAIL
-.8913
.71548
2.3222
CEN TC19/JWG1/PWI – 2012/03/22
TOTAL

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[2] EN 15751, *Automotive fuels — Fatty acid methyl ester (FAME) fuel and blends with diesel fuel — Determination of oxidation stability by accelerated oxidation method*

[3] ISO 6618, *Petroleum products and lubricants — Determination of acid or base number — Colour-indicator titration method*

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[6] EN 14214, *Liquid petroleum products — Fatty acid methyl esters (FAME) for use in diesel engines and heating applications — Requirements and test methods*

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