

CEN/TC19 2011 Conference



Development of Test Methods in CEN/TC19 Environment

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CEN/TC 19 is continuously following the evolution of test methods through its analytical working groups:

- JWG Flash point (with ISO/TC 28 and ISO/TC 35)
- WG 9 Chromatography
- WG 14 Cold flow properties of diesel fuel
- WG 15 Volatility of petrol
- WG 27 Elemental analysis
- WG 31 Contamination and filterability of diesel fuel
- WG 35 Ignition quality testing and correlation
- JWG 1 Vegetable fats and oils and their by-products for use in automotive fuels
(Joint working group with CEN/TC 307)



The activity of analytical WGs is driven by various needs:

- Updated or new requirements in fuel specifications due to the application of European directives
- Introduction of new fuel blends and blending components
- Revision of performance requirements of fuels

Activity carried out under WG 21 and WG 24 requests



Method development according to EN ISO 4259:2006

- Round robin test planning
- Estimation of test method precision
- Definition of working range



A preliminary work item is usually activated

- Choice of most suitable techniques, also according to the availability of instrumentations and to the required working range
- Analytical procedures (calibration, etc)
- Preliminary draft of the test method
- Stability and homogeneity of samples
- Ruggedness study



New work item – Round robin test

- Sample selection
- Call for participating labs
- RRT timing
 - sample preparation
 - sample shipping
 - measurements
 - statistical evaluation
 - approval of the test draft



Manganese content in petrol

EU Directive 2009/30: 6 mg/l max from 1-1-2011
 2 mg/l max from 1-1-2014

- Two suitable techniques: Flame AAS, ICP OES
- Different distribution of instruments in EU countries
- Both techniques with reasonable sensitivity (various ICP instrumentations)
- Calibration: MMT ? Organometallic Mn ?
- Samples: different types of petrol (E5, E10, MTBE, ETBE)

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Manganese content in petrol

Preliminary investigations

May-August 2009

Ruggedness study

September-October 2009

Round robin test

December-January 2010

Two different methods

prEN 16135 AAS

prEN 16136 ICP OES

Participants

12 AAS (6 countries)

19 ICP OES (7 countries)



Manganese content in petrol

Working range of both methods from about 2 to 8 mg/l

Precision

PrEN 16135 (AAS)

$$r = 0,05 X + 0,28$$

$$R = 0,13 X + 0,75$$

PrEN 16136 (ICP OES)

$$r = 0,04 X + 0,17$$

$$R = 0,17 X + 0,74$$

Both methods suitable at 6 mg/l, borderline at 2 mg/l

Revision needed to improve precision at 2 mg/l



Phosphorus content in FAME by ICP OES WI 019376

Working range of actual method EN 14107: 4 to 20 mg/kg

New test method investigated to extend working range to lower phosphorus contents as required by WG24/FAME TF

Use of internal standard

Use of real samples (not artificially doped with P species)

Possible extension of the procedure to sulfur determination



Phosphorus content in FAME by ICP OES WI 019376

Preliminary investigations November 2009 - April 2010

Ruggedness study May-June 2010

Round robin test September-November 2010

Participants 18 (10 countries)

Precision $r = 0,0255 X + 0,1782$
 $R = 0,1305 X + 0,9136$

Method applicable from about 2,5 mg/kg

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Sulfur test methods

EN ISO 20846 UVF

EN ISO 20884 WDXRF

New test method

EN ISO 13032 EDXRF

Revision required to allow the use to E10 petrol and B10 Diesel fuel

Technical aspects:

UVF Problems with cetane improvers

XRF Matrix effects due to oxygen content

WDXRF Extention to monochromatic WDXRF systems

EDXRF Very tight performance criteria

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Sulfur test methods

EN ISO 20846 UVF

EN ISO 20884 WDXRF

New test method

EN ISO 13032 EDXRF

Round robin test

November 2008 – February 2009

Participants

55 (Europe + 2 more continents !)

Methods updated and under Formal Vote ballot

UVF

Warning added for CI interference

WDXRF

Monochromatic systems included

EDXRF

Precision based on performance criteria



prEN 15492 Chloride and sulfate content in ethanol by IC

Very low chloride and sulfate content required in EN15376

ASTM D7319 and D7329 show suitable working range, but the precision (2R rule of ISO 4259) is not adequate for the European specification

Round robin test carried out using a procedure developed within WG27 (sample evaporation and ion chromatographic detection in aqueous solution)



prEN 15492 Chloride and sulfate content in ethanol by IC

Round robin test carried out with the participation of WG27 members, Customs, ethanol producers

2R limits according to ISO 4259 1,2 mg/kg chloride
0,5 mg/kg sulfate

prEN15492 updated ranges from about 1 mg/kg chloride
from about 1 mg/kg sulfate



WG9 - Oxygenates in E10 petrol (3,7 % oxygen)

Check of applicability of EN 1601, EN 13132 and EN ISO 22854 to E10:

- all three methods are *generally* fit for purpose
- preliminary precision defined for EN ISO 22854
- both EN ISO 22854 and EN 1601 to be revised



WG 31 Total contamination and filterability of Diesel fuels

Revision of EN 12662 required to include FAME and FAME blends, and to achieve a “robust” procedure for all sample types

Main discussion items:

- filter type and filtering medium
- FAME pretreatment
- tight criteria for filtration procedure



WG 31 Total contamination and filterability of Diesel fuels

Revision of EN 12662 Total contamination

Ruggedness study carried out in 2010

Round robin planning:

- sample selection
- preparation of homogeneous subsamples



WG 31 Total contamination and filterability of Diesel fuels

Development of a filterability test

The selected procedure is based on IP 387 (Filter Bloking Tendency) TM, with preliminary cold soak treatment of FAME samples and visual inspection before FBT measurement

Ruggedness study planned



WG 35 Ignition quality testing and correlation

- WG 24 requested (November 2009) a single EN test method for the ignition quality testing of distillate fuels based upon DCN (Derived Cetane Number) test methods
- WG 35 created May 2010, 14 experts (9 countries)
- Three different instruments available on the market:
the proposed test method will include all equipment types



WG 35 Ignition quality testing and correlation

- The proposed test method will be potentially included in EN 590
- The group is now working on the the feasibility of measuring DCN by comparison to blends of Cetane (EN ISO 5165) Primary Reference Fuels



Conclusions

Updating requirements for automotive fuels needs a relevant activity by analytical WGs.

The participation of experts to these WGs needed to enable the development of “robust” TMs.

Participation to round robin tests is crucial aspect of TM development within CEN/TC 19.