SLOVENSKI STANDARD
SIST-TP CEN/TR 15139:2005

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Naftni proizvodi in druge tekoļ ine ï Uporabnost preskusnih metod pri doloļ evanju ģvepla v naftnem in dizelskem gorivu

Petroleum products and other liquids - Applicability of test methods on sulfur determination in petrol and diesel fuel

Mineralölerzeugnisse und andere Flüssigkeiten - Anwendbarkeit von Prüfverfahren für die Schwefelbestimmung in Ottokraftstoffen und Dieselkraftstoffen

Produits pétroliers et autres liquides - Évaluation de méthodes d'essai de détermination de la teneur en soufre dans l'essence et le gazole

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Foreword

This Technical Report (CEN/TR 15139:2005) 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.

Introduction

During its 8th meeting held in London on 25 - 26 October 2000, CEN/TC 19/WG 27 "Elemental analysis of petroleum and related products" decided to carry out a second round robin, after the first performed in 1998 - 1999, to define the precision of new test methods in the range 1 mg/kg to 60 mg/kg sulfur. The range of sulfur content was selected to obtain definite and robust precision statements for future sulfur limits. The round robin was carried out in 2001.

The work has formed the basis for sulfur test method standards produced by the following organizations:

— ISO/TC 28 "Petroleum products", and

— CEN/TC 19 "Petroleum products, lubricants and related products".

1 Scope

This Technical Report summarises the activity carried out by CEN/TC 19 to define the precision of new test methods for the determination of low sulfur content in automotive fuels. The full description of the activity can be found in the Working Group Report completed in August 2002, which is an internal CEN/TC 19 document.

2 Test methods

WG 27 identified the most suitable instrumental methods to include in the round robin, also according to the experience gained in the round robin carried out in 1999. The methods available at that time and used in the assessment are listed below (see also Clause 12).

- EN ISO 14596 WDXRF (with internal standard) [1];
- ISO/CD 20846 UVF [2];
- ISO/CD 20847 EDXRF [3];
- ISO/CD 20884 WDXRF (without internal standard) [4];
- prEN ISO/DIS 16591 Oxidative microcoulometry [5].

3 Samples

Eight petrol and ten diesel samples with sulfur content from 1 mg/kg to 55 mg/kg were included in the round robin. Two samples were blends of FAME in diesel (5 % (*V/V*) FAME) and were included in the round robin to examine the applicability of the methods to FAME blends according to EN 590 specification [6].

Two samples (one petrol and one diesel) were considered as "quality control" samples, to check for accuracy of results, as sulfur content had been determined using Isotope Dilution Mass Spectrometry (ID-MS), the technique employed for the certification of element content in reference materials.

4 Laboratories

European laboratories were contacted to obtain a satisfactory participation for the methods listed above. A total of 102 applications from 11 countries were received. Table 1 shows the distribution of the techniques employed by the laboratories that effectively participated in the round robin.

Table 1 — Final list of participants

	WDXRF [a]		EDXRF		UVF	Microcoulometry
	High Power	Lower Power	Polarised	Non-polarised		
Laboratories	40	15	6	17	39	20

[a] High power instruments ≥ 3kW, lower power instruments ≤ 1 kW.

5 Evaluation of round robin results

The results received by the participants were firstly examined by the project leaders of each method for possible non compliance to the test methods (analytical outliers). The experts looked at the technical issues on the basis of the information submitted by the participants. They did not make judgement on the basis of the values submitted or on a statistical basis.

6 Statistical analysis

The statistical process used for the examination of the round robin was the methodology indicated in EN ISO 4259 [7]. Only linear models were chosen for the evaluation of repeatability and reproducibility. Global precision for all fuel samples or specific precision for each fuel was calculated according to the provisions already given in the precision clauses of the methods.

The following results were obtained (X is the mean of two results expressed in mg/kg):

EN ISO 14596 [1]:

All fuels (high power)	$r = 0{,}039\,9 \cdot X + 1{,}59$	$R = 0{,}067\,2 \cdot X + 2{,}69$
All fuels (lower power)	$r = 0{,}026\,9 \cdot X + 2{,}69$	$R = 0{,}042\,7 \cdot X + 4{,}27$

ISO/CD 20846 [2]:

Petrol	$r = 0{,}063\,1 \cdot X + 0{,}35$	$R = 0{,}174\,9 \cdot X + 0{,}96$
Diesel	$r = 0{,}055\,3 \cdot X + 0{,}55$	$R = 0{,}112\,0 \cdot X + 1{,}12$

ISO/CD 20847 [3]:

Petrol	$r = 0{,}031\,2 \cdot X + 9$	$R = 0{,}111\,6 \cdot X + 11$
Diesel	$r = 0{,}018\,8 \cdot X + 8$	$R = 0{,}016\,9 \cdot X + 12$

The precision data of ISO/CD 20847 were obtained by combining the results of the first and second round robin, to cover the complete sulfur range for the scope of the method.

ISO/CD 20884 [4]:

All fuels (high power)	$r = 0{,}024\,8 \cdot X + 1{,}7$	$R = 0{,}120\,1 \cdot X + 1{,}9$
All fuels (lower power)	$r = 0{,}040\,8 \cdot X + 2{,}0$	$R = 0{,}088\,9 \cdot X + 4{,}5$

prEN ISO/DIS 16591 [5]:

All fuels	$r = 0{,}045\,6 \cdot X + 1{,}14$	$R = 0{,}101\,8 \cdot X + 2{,}55$

7 Comparison between methods and accuracy

The comparison, using EN ISO 14596 as the reference method, showed statistically significant differences between the methods, but these differences were certainly very small and could be ignored from a practical point of view.

The accuracy of the methods was verified using the “quality control samples”. The results obtained for each test method for these samples were within the limits of the repeatability.

8 Applicability to FAME blends

The maximum difference observed between the sulfur content of the pure diesel fuel and that of the corresponding 5 % (*V/V*) FAME blends was in any case lower than the repeatability of each method.

9 Conclusions

9.1 EN ISO 14596: The precision found in the round robin for both high and lower power systems was better than that stated in the method, that refers to high power systems only.

9.2 ISO/CD 20846: The precision was better for diesel fuel than for petrol, as observed for other methods. The test method was found suitable for the determination of sulfur content ≥ 3 mg/kg (according to 2R rule of EN ISO 4259).

9.3 ISO/CD 20847: A substantial improvement was achieved with ISO/CD 20847 compared to EN ISO 8754 [8], and also compared to the results obtained in the 1998-1999 round robin. The current precision showed that the method is suitable for sulfur contents down to around 30 mg/kg. The results indicated that a new generation of EDXRF instruments (polarised source) has the potential to be used at lower sulfur content (< 10 mg/kg).

9.4 ISO/CD 20884: The results confirmed the precision stated in the method for low sulfur content, and showed that the new method is suitable for the determination of sulfur content ≥ 5 mg/kg (according to 2R rule of EN ISO 4259), when using high power instruments. On the other hand, the results showed that lower power instrumentation might not achieve adequate precision for sulfur contents of 10 mg/kg and below.

9.5 prEN ISO/DIS 16591: The precision found is quite close that stated in current ISO/CD 16591.

10 Recommendations for updating EN 228 and EN 590

According to the results obtained in the round robin, WG 27 recommended the following actions for the 2004 versions of the European specifications on petrol (EN 228 [9]) and diesel (EN 590 [6]):

— EN ISO 14596 to be replaced by ISO/DIS 20884. The new method does not require the addition of the internal standard and shows satisfactory precision at 50 mg/kg and 10 mg/kg;

— EN 24260 [10] to be replaced by ISO/DIS 20846. UVF method, also based on sample combustion, shows satisfactory precision at 50 mg/kg and 10 mg/kg;

— EN ISO 8754 to be replaced by ISO/DIS 20847. EN ISO 8754 cannot be used at 350 mg/kg and 150 mg/kg (2R rule of EN ISO 4259 is not fulfilled), while ISO/DIS 20847 can determine down to 30 mg/kg sulfur.