SLOVENSKI STANDARD
SIST-TP CEN/TR 15745:2009

01-januar-2009

Tekoļ i naftni proizvodi - Doloļ evanje vrste ogljikovodikov in oksigenatov z multidimenzionalno plinsko kromatografsko metodo - Medlaboratorijsko primerjalno poroļ ilo

Liquid petroleum products - Determination of hydrocarbon types and oxygenates via multidimensional gas chromatography method - Round Robin research report

Flüssige Mineralölerzeugnisse - Bestimmung der Kohlenwasserstoffgruppen und sauerstoffhaltigen Verbindungen mit multidimensionalen gaschromatographischen Verfahren - Round Robin Forschungsbericht

Produits pétroliers liquides - Détermination des groupes d'hydrocarbures et de la teneur en composé oxygénés par méthode par chromatrographie multidimensionnelle en phase gazeuse - Rapport de recherche interlaboratoire

Ta slovenski standard je istoveten z: **CEN/TR 15745:2008**

ICS:

75.160.20 Tekoļ a goriva Liquid fuels

SIST-TP CEN/TR 15745:2009 **en,fr**

TECHNICAL REPORT

RAPPORT TECHNIQUE

TECHNISCHER BERICHT

CEN/TR 15745

November 2008

ICS 75.160.20

English Version

Liquid petroleum products - Determination of hydrocarbon types and oxygenates via multidimensional gas chromatography method - Round Robin research report

Produits pétroliers liquides - Détermination des groupes d'hydrocarbures et de la teneur en composés oxygénés par méthode par chromatrographie multidimensionnelle en phase gazeuse - Rapport de recherche interlaboratoires

Flüssige Mineralölerzeugnisse - Bestimmung der Kohlenwasserstoffgruppen und sauerstoffhaltigen Verbindungen mit multidimensionalen gaschromatographischen Verfahren - Round Robin Forschungsbericht

This Technical Report was approved by CEN on 30 March 2008. It has been drawn up by the Technical Committee CEN/TC 19.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. CEN/TR 15745:2008: E

Contents

Page

Foreword

This document (CEN/TR 15745:2008) 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Report: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

In 2004, the company AC Analytical Controls [1] conducted a Performance Monitoring Program on the AC Reformulyzer™. This is a kind of crosscheck program where customers analyse samples distributed by the company and then report the analysis results. The company checks the analytical performance of the instruments, keeping in mind the possible analytical errors that can occur. Because raw data are reported (chromatogram and data for each carbon number/group), a detailed review can be made. The company informs a customer when the instrument performance is inadequate and where possible provides information and instructions to improve the performance.

The intention was to get a precision statement for oxygenates that were not included in EN 14517, but that are listed in EN 228. Besides this, the performance for other properties (aromatics, olefins, benzene) has been determined.

More information on the review of the data is available from the monitoring, but this technical report focuses on oxygenates. Results for other properties (aromatics, olefins, benzene) are listed in the tables but are not discussed in detail here. Also the evaluation for outliers is done on oxygenates only, not on the other properties.

[1] Postal address: P.O. Box 10054, 3004 AB Rotterdam, The Netherlands, E-mail: acbv@analytical-controls.com, Web: www.analytical-controls.com.

1 Scope

This Technical Report presents the study on the application of EN 14517 to other oxygenates. This report supports an extension of the scope of the method, which has been explicitly requested by ISO/TC 28 at the time of revision of EN 14517 and was agreed to result in the parallel Standard EN ISO 22854.

This report is published as background information to judge the approval of the use of the method for the determination of all oxygenates as mentioned in the European Fuels Directive. Next, this report should support the use of multidimensional chromatography as the method for disputes on oxygenates in EN 228.

NOTE For the purposes of this document, the term "% (*V/V*)" is used to represent the volume fraction.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 4259, *Petroleum products - Determination and application of precision data in relation to methods of test (ISO 4259:2006)*

3 Participating labs

Labs that have participated in the 2005 to 2006 Round Robin work are mentioned in Table 1.

4 Sample set

The sample set as given in Table 2 has been used.

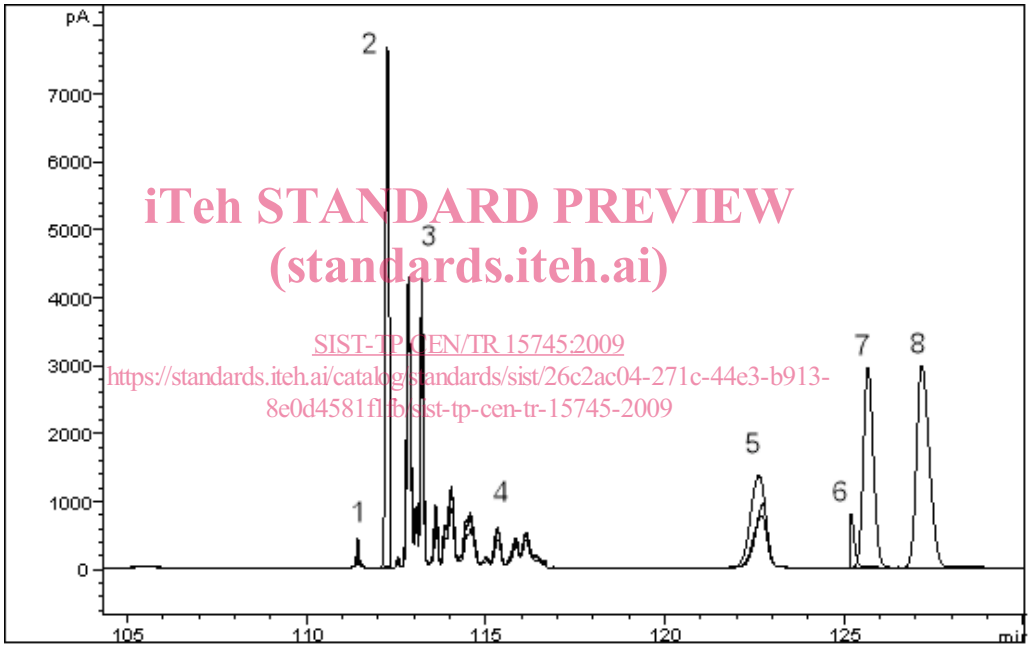
Table 1 — Participating labs

Company / lab	Country
Umweltbunderambt	Austria
Total Raffinaderij	Belgium
BRC	Belgium
Statoil Kalundborg	Denmark
Fortum	Finland
ExxonMobil	France
Total CReG	France
Shell Petit-Couronne	France
PCK	Germany
BP Gelsenkirchen	Germany
Total Leuna	Germany
SGS Speyer	Germany
Bayernoil	Germany
BP	Germany
Opel	Germany
Shell Heide	Germany
Hellenic Petroleum	Greece
MOL RT	Hungary
MOL	Hungary
ENI Gela	Italy
ENI, Euron	Italy
ENI Agip Roma	Italy
ENI Agip	Italy
ENI Agip Sanazzaro	Italy
ENI R&M Livorno	Italy
SGS Spijkenisse	Netherlands
Nerefco	Netherlands
Total	Netherlands
Shell Pernis	Netherlands
Slovnaft	Slovak Republic
Repsol	Spain
BP Castellon	Spain
ConocoPhilips	UK
Intertek Sunbury	UK
Total	UK
Shell Global Solutions	UK

Table 2 — Sample set of the Round Robin

Sample	Oxygenate	Oxygenate level % (*V/V*)	Aromatics % (*V/V*)	Olefins % (*V/V*)	Benzene % (*V/V*)
1	MTBE	11	32	24	0,64
2	t-Butanol Methanol	6,8 3	19	8,5	0,54
3	i-Propanol MTBE	10,3 8,4	23	14,6	0,70
4	i-Butanol MTBE	10,1 0,25	22	12,4	0,81

Figure 1 gives an overview of the present oxygenates in the sample.



Key

1 Methanol
2 i-Propanol
3 C9 Aromatics
4 C10 Aromatics
5 High boiling aromatics
6 i-Propanol
7 t-Butanol
8 i-Butanol

Figure 1 — Overlaid section of chromatogram of samples with identified components

5 Results from the round robin test

5.1 Sample 1

The results of measurement on sample 1 returned are given in Table 3. The overall results (average and standard deviation) are given at the end of the table.

Table 3 — Results of sample 1 in % (*V/V*)

Lab [a]	Aromatics		Olefins		Benzene		MTBE	
	1	2	1	2	1	2	1	2
1	32,43	32,18	22,76	23,02	0,66	0,65	11,80	11,56
2	32,29	32,44	21,81	21,69	0,64	0,65	11,87	11,89
3	32,06	32,14	18,91	19,10	0,64	0,64	11,26	11,28
4	31,65	31,59	24,22	24,21	0,65	0,64	11,57	11,60
5	32,01	31,81	24,01	23,40	0,65	0,65	11,37	11,27
6	33,48	34,16	19,99	18,55	0,60	0,62	11,11	12,29
7	30,96		24,94		0,61		11,26	
8	32,65	32,46	22,39	22,81	0,66	0,66	11,75	11,74
9	31,46	31,49	20,33	20,27	0,64	0,64	11,43	11,43
10	33,88	34,18	22,83	23,24	0,67	0,66	11,57	11,51
11	35,42	35,46	23,90	24,11	0,70	0,69	11,76	11,69
12	31,10	31,09	19,46	19,82	0,65	0,65	11,26	11,25
13	31,15	30,92	22,45	23,39	0,64	0,64	11,35	11,43
14	*32,36*	*32,58*	*31,51*	*31,65*	*0,67*	*0,66*	*3,51*	*3,46*
15	35,44	35,60	23,26	23,70	0,69	0,69	11,86	11,79
16	31,38		25,56		0,63		11,52	
17	30,38	30,43	21,00	22,15	0,63	0,63	11,23	11,27
18	*33,15*	*32,91*	*22,47*	*22,91*	*0,67*	*0,65*	*9,51*	*9,02*
19	32,90	33,11	21,60	21,97	0,61	0,61	12,01	12,11
20	31,64		23,93		0,65		11,75	
21	31,25	31,34	24,42	24,35	0,65	0,65	11,57	11,55
22	30,95	30,98	24,62	24,69	0,63	0,63	11,27	11,23
23	31,58	31,69	25,48	25,49	0,55	0,55	11,51	11,54
24	32,24	34,02	22,72	23,51	0,66	0,63	11,57	11,02
26	28,54		21,67		0,64		11,31	
27	32,11	31,59	20,66	21,80	0,66	0,66	11,59	11,72
28	32,86	32,85	24,85	25,55	0,58	0,58	11,07	11,11
29	32,20	32,12	21,13	21,19	0,64	0,64	11,08	11,11
30	31,89	31,92	20,58	20,56	0,65	0,64	11,51	11,45
31	31,20	31,01	15,58	16,20	0,61	0,62	11,24	11,37
32	*32,63*	*32,63*	*20,74*	*20,94*	*0,65*	*0,65*	*9,95*	*9,99*
33	34,21		20,89		0,69		12,17	
34	32,01		24,36		0,66		11,65	
35	31,48		20,42		0,68		12,16	
44	32,82	32,80	21,44	21,00	0,67	0,68	11,78	11,94
Average	32,27		22,51		0,64		11,16	
Stdev	1,31		2,69		0,03		1,51	

[a] Greyed cells are classified as an outlier for oxygenates. The results for an entire lab were removed if an outlier in the oxygenates was found.

After outlier removal (indicated by the grey zones and cells) the following results are determined:

	Aromatics	Olefins	Benzene	MTBE
Average	32,23	22,24	0,64	11,53
Stdev	1,36	2,22	0,03	0,30

NOTE 1 Labs with chromatographic issues with MTBE – 14, 18, 32 – have been rejected (see Clause 6.1).

NOTE 2 Second analysis of labs 6 and 24 is rejected on Hawkins test for MTBE.

5.2 Results sample 2

The results of measurement on sample 2 returned are given in Table 4. The overall results are given at the end of the table.

After outlier removal (greyed cells in Table 4) the following can be determined as follows:

	Aromatics	Olefins	Benzene	t-Butanol	Methanol
Average	18,95	8,60	0,55	6,74	2,12
Stdev	0,51	0,48	0,02	0,17	1,21

NOTE Labs that failed to identify t-Butanol have been rejected (see 6.3). Lab 6 has been rejected for t-Butanol as Cochran outlier.