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

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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 recherches interlaboratoires

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

This Technical Report was approved by CEN on 24 February 2015. It has been drawn up by the Technical Committee CEN/TC 19.

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Foreword

This document (CEN/TR 15475:2015) 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.

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.

This document supersedes CEN/TR 15745:2008.

The second edition of this document includes Round Robin data generated in 2012 that led to revision of EN ISO 22854.

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 [2], 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.

The precision data obtained from this program were used to develop the EN ISO 22854 method which was published in 2008 [3].

In 2010 another Round Robin was organized to establish a test method to determine the oxygenated components in ethanol automotive fuel (E85). Components such as ethers, C3-C5 alcohols and ethanol could be made part of an E85 specification.

Four methods were tested:

A. EN ISO 22854 modified (with sample dilution)

B. EN 1601 modified (with sample dilution)

C. Capillary column method (2 columns in series, UNGDA method)

D. Capillary column method (2 separate columns, Suedzucker method)

Only method A with sample dilution had enough participants to derive a precision statement. The dilution step was needed to lower the ethanol content in the sample to values below 20 % (*V*/*V*).

The Round Robin was carried out by TC 19/WG 9 and the results were evaluated conform EN ISO 4259. As methods B, C and D did not get enough participants a 2nd ILS was carried out to see if more data could be obtained for these methods. The details of these Round Robin Tests are added as Appendix A and B to this Research Report.

1) Postal address: AC Analytical Controls, Innsbruckweg 35 3047 AG Rotterdam, The Netherlands, E-mail:sales.netherlands@paclp.com, Web: www.paclp.com.

1 Scope

This Technical Report presents the study on the application of EN 14517 [2] 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 [3].

This Technical 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. This Technical Report should also support the use of multidimensional chromatography as the method for disputes on oxygenates in EN 228 [1].

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

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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)*

3 Participating laboratories

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

Table 1 — Participating laboratories

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

Laboratories that have participated in the second RR work are presented in Annex B.

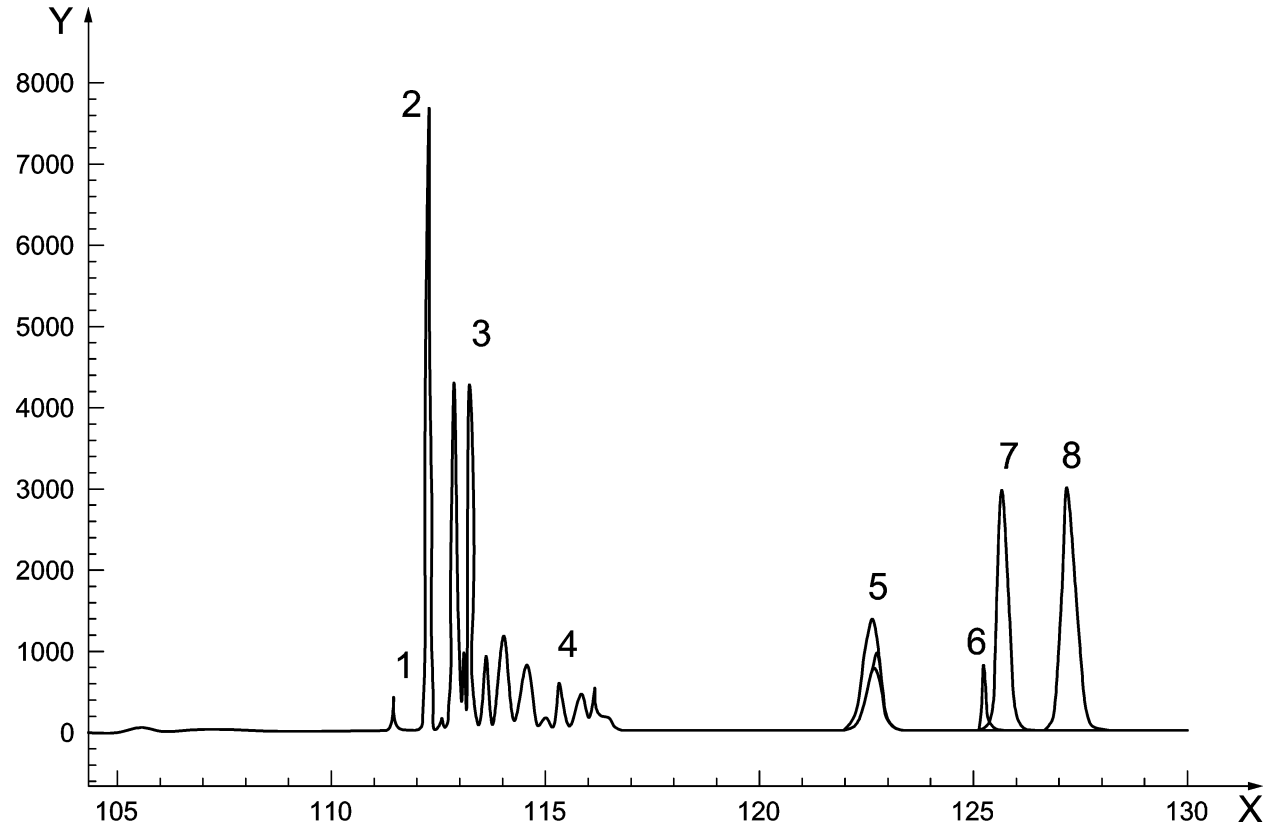
4 Sample set

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

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

X	min	4	C10 Aromatics
Y	pA	5	High boiling aromatics
1	Methanol	6	i-Propanol
2	i-Propanol	7	t-Butanol
3	C9 Aromatics	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

Lab [a]	Aromatics		Olefins		Benzene		MTBE	
	1	2	1	2	1	2	1	2
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 results as in Table 4 are determined.

Table 4 — Results

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

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

NOTE 2 Second analysis of laboratories 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 5. The overall results are given at the end of the table.

Table 5 — Results of sample 2 in % (*V/V*)

Lab [a]	Aromatics		Olefins		Benzene		t-Butanol		Methanol	
	1	2	1	2	1	2	1	2	1	2
1	19,26	19,36	8,77	8,66	0,55	0,56	6,94	7,02	1,32	1,36
2	19,27	19,22	8,29	8,43	0,54	0,55	6,97	6,90	0,60	0,60
3	18,52	18,56	9,01	8,99	0,53	0,53	6,42	6,41	3,82	3,82
4	19,08	19,05	8,51	8,54	0,55	0,55	6,72	6,73	1,50	1,56
5	19,12	19,05	8,83	8,79	0,56	0,56	6,82	6,90	1,66	1,71
6	*19,97*	*19,68*	*6,40*	*7,27*	*0,44*	*0,44*	*7,84*	*7,78*	*0,00*	*0,00*
7	18,69	18,59	9,04	9,01	0,53	0,53	6,68	6,71	0,93	1,10
8	18,80	18,76	8,15	8,19	0,54	0,54	6,64	6,65	4,36	4,42
9	19,31	19,28	8,87	8,95	0,56	0,56	6,82	6,87	0,38	0,33
10	19,85	20,01	8,23	8,21	0,58	0,57	6,84	6,88	0,87	0,96
12	18,70	18,71	9,15	9,16	0,56	0,57	6,75	6,77	2,48	2,60

Lab [a]	Aromatics		Olefins		Benzene		t-Butanol		Methanol	
	1	2	1	2	1	2	1	2	1	2
13	18,95	18,92	9,06	9,05	0,55	0,55	6,62	6,63	1,53	1,65
14	18,80	19,13	8,77	8,62	0,55	0,53	6,97	7,14	1,98	2,06
15	20,07	20,11	8,35	8,33	0,56	0,56	6,97	7,00	1,51	1,65
16	18,65	19,15	8,97	9,00	0,53	0,53	6,80	6,73	4,15	4,06
17	18,67	18,61	9,62	9,51	0,55	0,55	6,79	6,77	1,18	1,32
18	*18,66*	*18,81*	*7,78*	*7,44*	*0,52*	*0,53*	*0,00*	*0,00*	*3,68*	*3,76*
19	*20,39*	*19,71*	*8,32*	*8,04*	*0,54*	*0,54*	*7,19*	*0,00*	*0,00*	*0,00*
20	18,69		8,33		0,54		6,76		2,71	
21	18,81	18,71	8,18	8,35	0,55	0,55	6,76	6,73	2,37	2,48
22	*19,67*	*19,48*	*8,81*	*8,85*	*0,54*	*0,53*	*0,00*	*0,00*	*0,00*	*0,00*
23	19,22	19,14	8,86	9,01	0,50	0,50	6,83	6,85	1,54	1,36
24	*19,74*	*18,97*	*7,77*	*8,37*	*0,50*	*0,54*	*0,00*	*0,00*	*0,90*	*0,89*
25	17,40	17,28	8,16	8,06	0,55	0,55	6,75	6,73	2,16	2,37
26	18,78	18,93	7,87	7,38	0,54	0,54	6,62	6,58	4,01	3,98
27	18,65	18,53	8,28	8,25	0,55	0,55	6,76	6,76	2,45	2,53
28	18,76	18,71	7,92	7,88	0,53	0,53	6,36	6,34	3,67	3,72
29	18,74	18,93	8,63	8,56	0,54	0,54	6,59	6,52	3,74	3,72
30	*18,41*	*18,35*	*8,33*	*8,23*	*0,54*	*0,52*	*0,00*	*0,00*	*1,32*	*1,33*
31	19,09	19,16	9,16	9,15	0,54	0,54	6,63	6,60	1,06	1,16
32	*18,27*	*18,29*	*8,30*	*8,29*	*0,53*	*0,53*	*0,00*	*0,00*	*3,90*	*3,91*
33	19,47		7,54		0,56		6,71		0,00	
34	19,16	19,03	8,74	8,72	0,56	0,55	6,73	6,73	1,67	1,83
35	*19,49*	*19,39*	*7,80*	*7,94*	*0,53*	*0,54*	*0,00*	*0,00*	*0,00*	*0,00*
44	*18,98*	*18,84*	*7,92*	*7,92*	*0,55*	*0,55*	*0,00*	*0,00*	*0,00*	*0,00*
Average	19,01		8,44		0,54		5,29		1,85	
Stdev	0,55		0,57		0,02		2,85		1,38	

[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 (greyed cells in Table 5) the results can be determined as in Table 6.

Table 6 — Results

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

5.3 Results sample 3

The results of measurement on sample 3 returned are given in Table 7. The overall results are given at the end of the table.

Table 7 — Results of sample 3 in % (*V/V*)

Lab [a]	Aromatics		Olefins		Benzene		i-Propanol		MTBE	
	1	2	1	2	1	2	1	2	1	2
1	22,67	22,82	14,51	14,40	0,70	0,71	9,74	10,03	8,35	8,44
2	21,69	21,49	13,66	13,81	0,65	0,66	4,83	4,86	8,31	8,33
3	22,64	22,63	15,45	15,46	0,69	0,69	9,96	9,97	8,11	8,09
4	22,21	22,21	14,56	14,62	0,70	0,70	10,41	10,44	8,48	8,48
5	22,42	22,28	14,69	14,79	0,70	0,70	10,55	10,61	8,39	8,42
6	22,39	22,50	13,08	13,07	0,63	0,63	10,82	10,85	8,44	8,47
7	21,96	21,87	15,17	15,24	0,67	0,68	9,71	9,85	8,52	8,38
8	23,00	22,99	14,27	14,54	0,71	0,71	10,61	10,64	8,33	8,32
9	22,53	22,40	15,21	15,00	0,70	0,68	9,51	9,62	8,31	8,35
10	23,50	23,78	13,66	13,72	0,71	0,71	10,17	10,17	8,13	8,10
11	23,11	22,91	13,84	13,92	0,71	0,71	9,25	9,25	8,21	8,30
12	22,26	22,29	15,41	15,60	0,72	0,71	10,07	10,08	8,23	8,19
13	21,90	21,92	15,28	15,36	0,69	0,70	10,40	10,46	8,51	8,38
14	22,61	22,66	19,22	19,40	0,70	0,69	10,66	10,69	3,05	2,94
15	23,49	23,59	14,36	14,30	0,71	0,72	9,85	9,98	8,65	8,65
16	23,38	23,11	15,30	15,60	0,69	0,69	10,47	10,51	8,08	8,20
17	21,47	21,23	16,12	16,14	0,69	0,68	0,00	0,00	8,28	8,20
18	23,08	22,99	13,97	13,95	0,70	0,69	0,00	0,00	5,97	6,14
19	23,44	23,49	13,73	13,89	0,69	0,68	6,57	6,38	10,30	10,71
20	22,77	22,74	14,61	14,58	0,70	0,70	10,34	10,33	8,36	8,37
21	22,26	22,41	14,48	14,55	0,71	0,71	10,23	10,29	8,40	8,46
22	28,62	28,62	16,21	16,24	0,73	0,74	0,00	0,00	8,77	8,68
23	22,17	22,32	15,28	15,36	0,62	0,61	8,95	8,99	8,59	8,43
24	27,50	27,12	14,90	15,28	0,72	0,73	0,00	0,00	10,50	10,44
25	19,04	19,06	4,97	4,88	0,70	0,71	10,45	10,48	8,11	8,11
26	19,74		12,90		0,72		10,14		8,35	
27	22,03	22,07	14,10	14,10	0,71	0,70	10,75	10,74	8,28	8,26
28	22,56	22,60	14,30	14,34	0,68	0,68	10,61	10,61	7,99	7,97
29	22,85	22,75	14,80	14,80	0,70	0,70	10,32	10,36	7,99	8,01
30	24,18	23,83	14,69	14,61	0,71	0,70	0,00	0,00	8,39	8,37
31	22,07	22,05	15,29	15,28	0,67	0,67	10,39	10,42	8,43	8,28

Lab [a]	Aromatics		Olefins		Benzene		i-Propanol		MTBE	
	1	2	1	2	1	2	1	2	1	2
32	22,95	22,88	14,40	14,40	0,70	0,70	0,00	0,00	7,23	7,21
33	25,54		13,44		0,73		0,00		8,68	
34	22,28	22,30	14,88	14,85	0,71	0,71	10,52	10,54	8,71	8,49
35	28,60	28,72	14,86	14,91	0,75	0,75	0,00	0,00	9,11	8,99
44	25,01	25,06	14,31	14,22	0,73	0,74	0,00	0,00	8,73	8,76
Average	23,02		14,49		0,70		7,57		8,25	
Stdev	1,89		1,94		0,03		4,39		1,13	

[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 (greyed cells in Table 7) the results can be determined as in Table 8:

Table 8 — Results

	Aromatics	Olefins	Benzene	i-Propanol	MTBE
Average	22,36	14,42	0,69	10,24	8,32
Stdev	0,91	2,24	0,02	0,47	0,18

NOTE Laboratories that failed to identify i-Propanol or one of the i-Propanol peaks have been rejected (see 6.4).

5.4 Results sample 4

The results of measurement on sample 4 returned are given in Table 9. The overall results are given at the end of the table.

Table 9 — Results of sample 4 in % (*V/V*)

Lab [a]	Aromatics		Olefins		Benzene		i-Butanol		MTBE	
	1	2	1	2	1	2	1	2	1	2
1	22,48	22,88	12,54	12,59	0,83	0,84	10,19	10,34	0,23	0,24
2	22,39	22,26	12,08	12,21	0,79	0,80	10,19	10,03	0,53	0,51
3	22,20	22,24	13,18	13,17	0,81	0,81	9,90	9,91	0,18	0,19
4	22,06	22,05	12,47	12,47	0,82	0,81	9,92	9,94	0,23	0,28
5	22,26	22,11	12,54	12,57	0,82	0,82	10,16	10,09	0,28	0,28
6	21,60	21,80	11,59	11,61	0,81	0,80	10,04	10,09	0,32	0,32
7	21,69	21,54	12,79	12,83	0,78	0,78	9,85	9,84	0,32	0,33
8	22,42	22,38	12,42	12,45	0,82	0,82	10,07	10,09	0,23	0,22
9	22,38	22,54	12,76	12,65	0,83	0,82	10,05	10,15	0,28	0,30
10	24,17	23,83	11,83	11,72	0,83	0,81	9,96	9,87	0,23	0,23
11	23,70	23,73	11,95	11,84	0,86	0,85	0,00	0,00	0,29	0,29
12	21,90	21,92	12,56	12,65	0,83	0,83	9,97	9,97	0,24	0,24
13	22,28	22,15	12,74	12,92	0,82	0,82	10,01	9,96	0,34	0,36
14	22,20	22,32	12,52	12,31	0,82	0,81	10,09	10,23	0,23	0,23
15	23,57	23,62	12,07	12,02	0,84	0,84	10,67	10,73	0,25	0,23
16	21,90	21,93	13,24	13,23	0,80	0,80	0,00	0,00	0,00	0,00
17	20,50	20,56	13,51	13,42	0,78	0,78	0,00	0,00	0,25	0,25
18	23,35	22,89	11,81	11,99	0,82	0,82	0,00	0,00	10,68	10,49
19	23,48	23,55	12,23	12,00	0,80	0,80	10,55	10,62	0,24	0,24
20	22,02	22,06	12,42	12,29	0,80	0,80	9,94	9,96	0,25	0,25
21	21,87	22,03	12,33	12,28	0,82	0,82	9,96	10,02	0,28	0,23
22	21,59	21,73	12,52	12,47	0,78	0,78	0,00	0,00	0,22	0,22
23	22,20	22,31	12,82	12,90	0,74	0,72	10,12	10,51	0,32	0,31
24	24,62	23,49	11,47	12,39	0,77	0,83	0,00	0,00	0,39	0,39
25	19,91	19,90	5,51	5,56	0,80	0,79	0,00	0,01	0,24	0,24
26	22,49	22,54	12,15	12,13	0,81	0,81	10,07	10,20	0,21	0,22
27	21,57	21,58	12,23	12,24	0,82	0,82	10,02	10,01	0,23	0,23
28	22,55	22,63	12,18	12,16	0,80	0,80	9,90	9,93	0,21	0,21
29	22,00	22,20	12,50	12,22	0,80	0,80	0,00	0,00	0,18	0,19
30	22,06	22,09	12,68	12,60	0,81	0,81	0,00	0,00	10,54	10,52
31	21,71	21,76	12,36	12,12	0,78	0,77	0,00	0,00	0,31	0,23

Lab [a]	Aromatics		Olefins		Benzene		i-Butanol		MTBE	
	1	2	1	2	1	2	1	2	1	2
32	22,09	22,12	12,37	12,54	0,80	0,80	0,00	0,00	0,00	0,00
33	22,75		11,62		0,83		10,15		0,27	
34	22,12	22,22	12,75	12,71	0,82	0,82	9,95	10,00	0,32	0,31
35	22,84	22,90	12,30	12,20	0,82	0,82	0,00	0,00	0,24	0,23
44	22,67	22,41	11,85	11,97	0,83	0,83	0,00	0,00	10,65	10,61
Average	22,31		12,20		0,81		6,40		1,12	
Stdev	0,84		1,22		0,02		4,90		2,90	

[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 (greyed cells) the results can be determined as in Table 10.

Table 10 — Results

	Aromatics	Olefins	Benzene	i-Butanol	MTBE
Average	22,38	12,39	0,81	10,09	0,26
Stdev	0,61	0,39	0,02	0,22	0,04

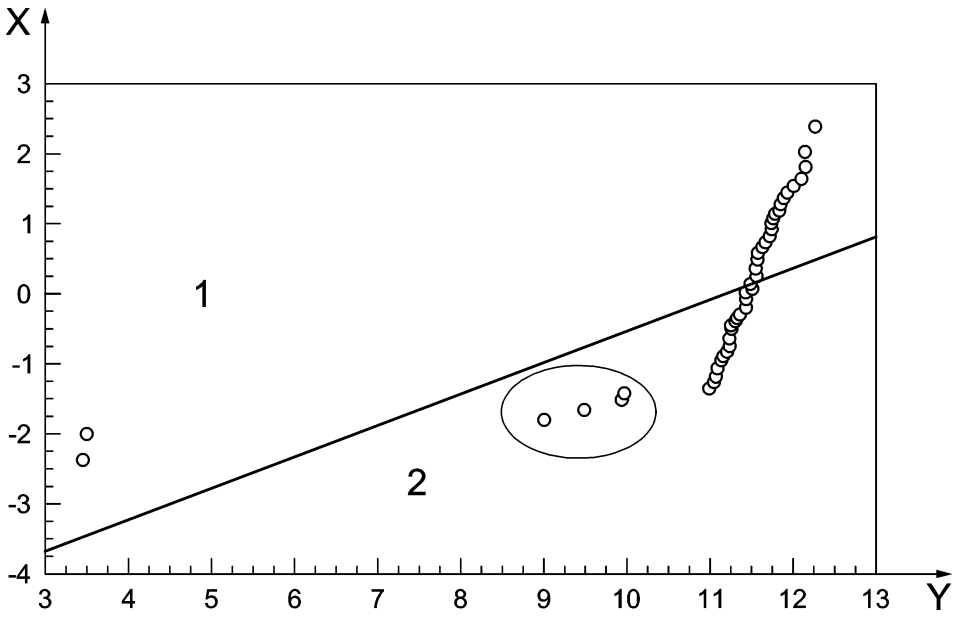
NOTE 1 Laboratories that failed to identify i-Butanol have been rejected.

NOTE 2 Lab 2 is Cochran outlier on MTBE.

6 Review of the data

6.1 MTBE

The results are given in Figure 2 and Figure 3.



Key

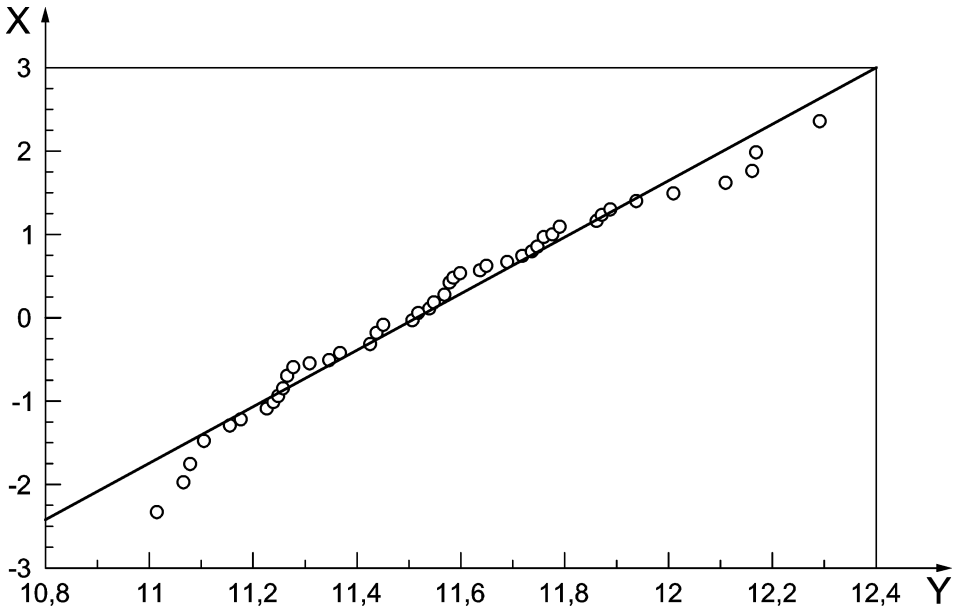
X Expected Normal Value

Y MTBE content, % (*V/V*)

1 Lab 14 – EthAlc trap separation too high, Break through to C4 Olefins

2 Laboratories 18, 32 – Precolumn too low. Elution in first and second aromatics fraction. Second fraction identified as propanol / t-butanol

Figure 2 — sample 1, n-Probability of MTBE - all data



Key

X Expected Normal Value

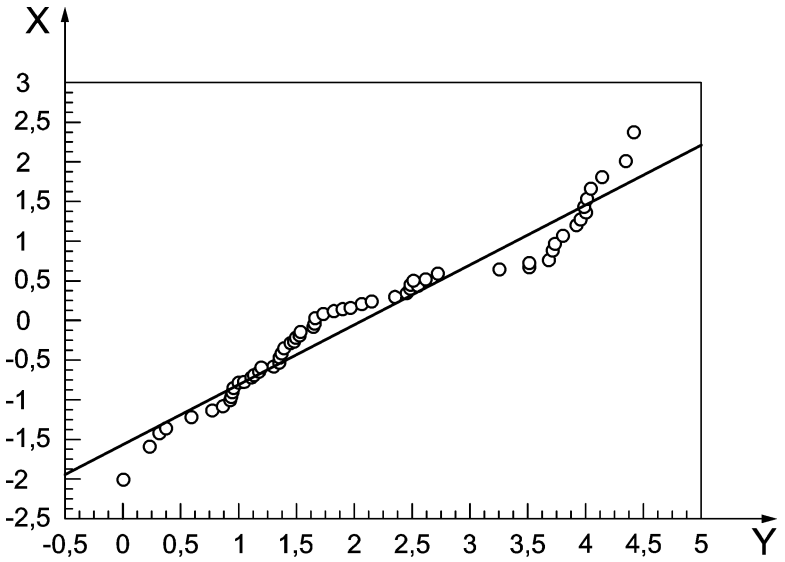
Y MTBE content, % (*V/V*)

Figure 3 — Sample 1, n-Probability of MTBE - laboratories 14, 18, 32 removed

6.2 Methanol

Methanol results have been found to vary from near zero to the expected level of the sample. The high response factor of methanol is a contributing factor. The high variance may be due to the pre-column not being able to retain methanol. This component is not routinely analysed since it does not occur in production samples at high levels. When found it is usually a remainder of the MTBE production process. The instrument should be tuned for this component with a gravimetric standard.

The results are plotted in Figure 4. No results have been omitted from the calculation other than the results where no methanol was found at all.



Key

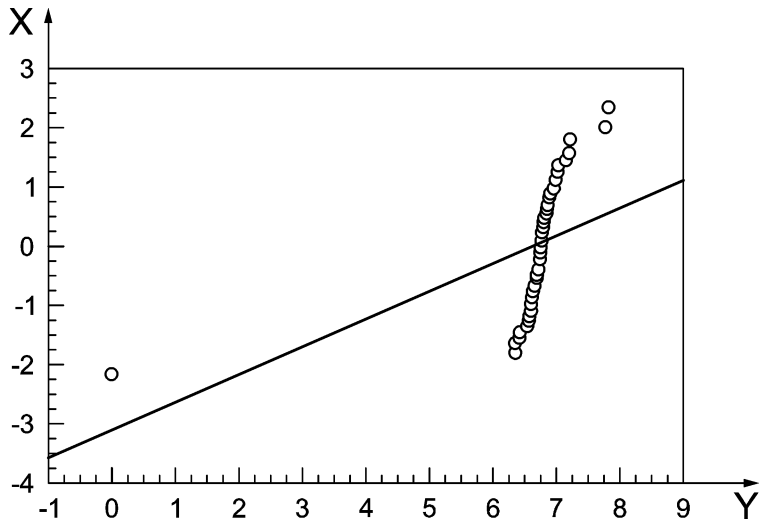
X Expected Normal Value

Y Methanol content, % (*V/V*)

Figure 4 — Sample 2, n-Probability of Methanol

6.3 t-Butanol

The most common error has been that t-Butanol was not identified properly. It has been identified as one of the oxygenated components that could elute in this part of the chromatogram such as n-Butanol.

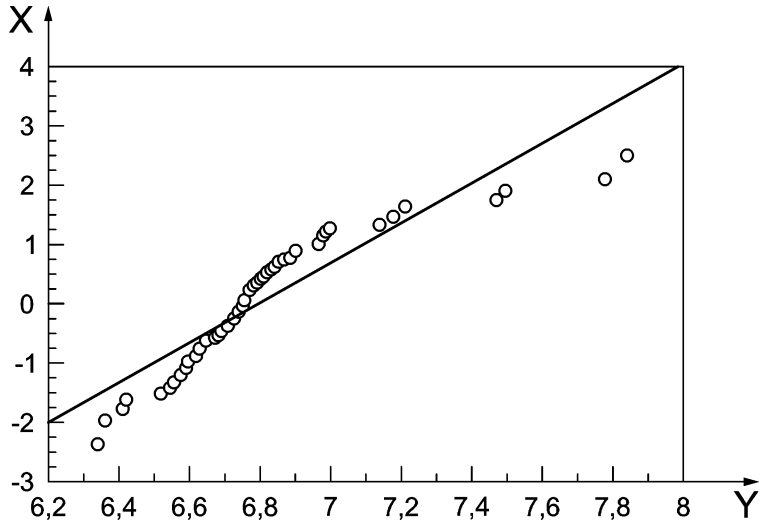


Key

X Expected Normal Value

Y t-Butanol content, % (*V/V*)

Figure 5 — Sample 2, n-Probability t-Butanol all data



Key

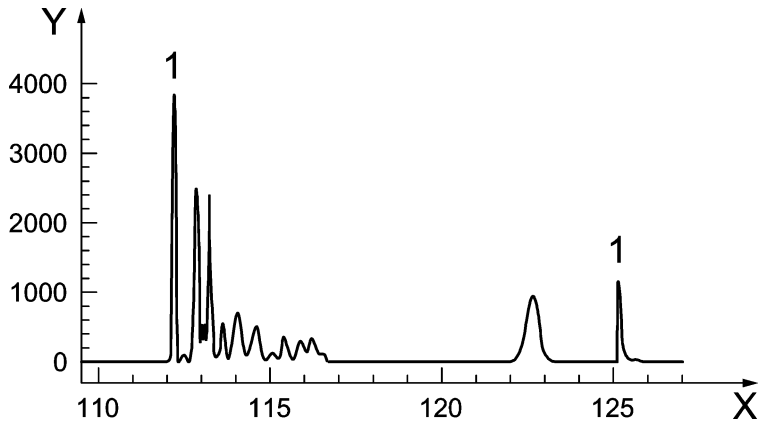
X Expected Normal Value

Y t-Butanol content, % (*V/V*)

Figure 6 — Sample 2, n-Probability t-Butanol - unidentified removed

6.4 i-Propanol

On many instruments, i-Propanol has been cut into two peaks (see Figure 7). In this case, it often happens that at least one of the peaks is misidentified. With a normal probability plot it becomes clear that a normal distribution is not followed.



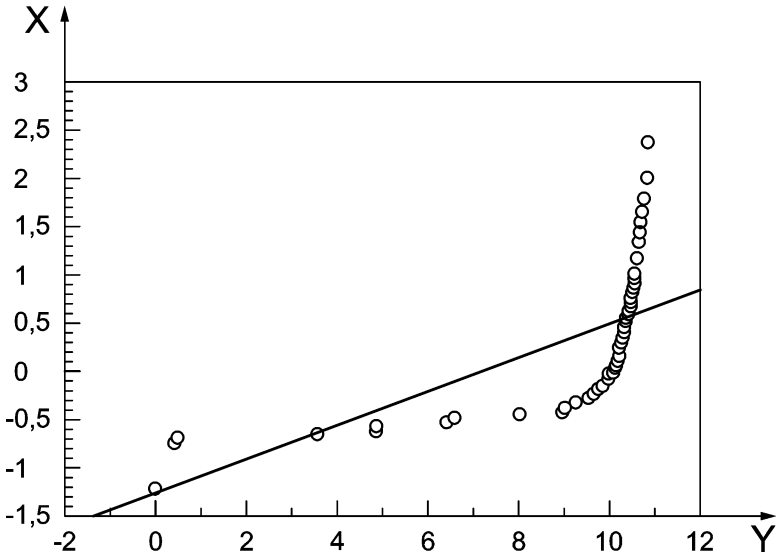
Key

X min

Y PA

1 i-Propanol peak cut in two

Figure 7 — Example of an i-propanol plot

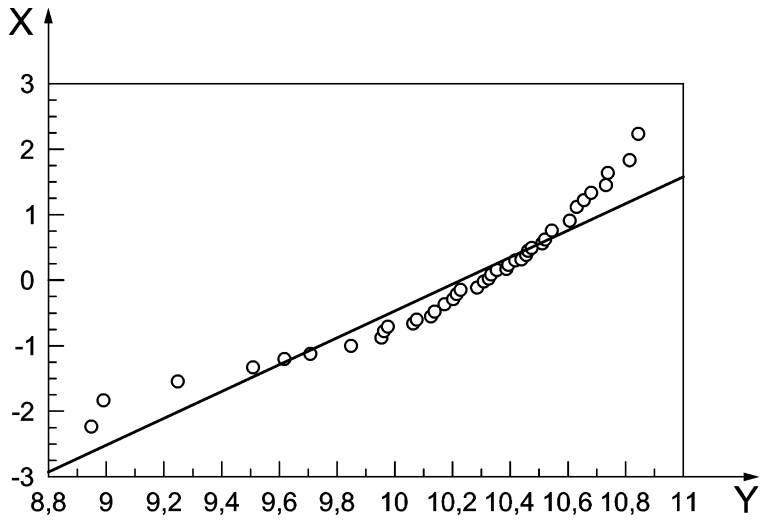


Key

X Expected Normal Value

Y i-Propanol content, % (*V/V*)

Figure 8 — Sample 3, n-Probability i -Propanol - all data



Key

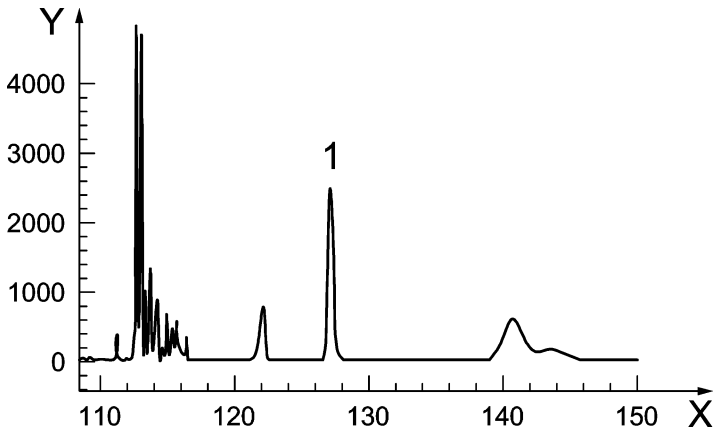
X Expected Normal Value

Y i-Propanol content, % (*V/V*)

Figure 9 — Sample 3, i-Propanol - most partially identified data removed

6.5 i-Butanol

i-Butanol has little chance to be cut into several peaks (see Figure 10). However, the peak has been identified as MTBE, Ethanol, n-Propanol, t-Butanol and s-Butanol.



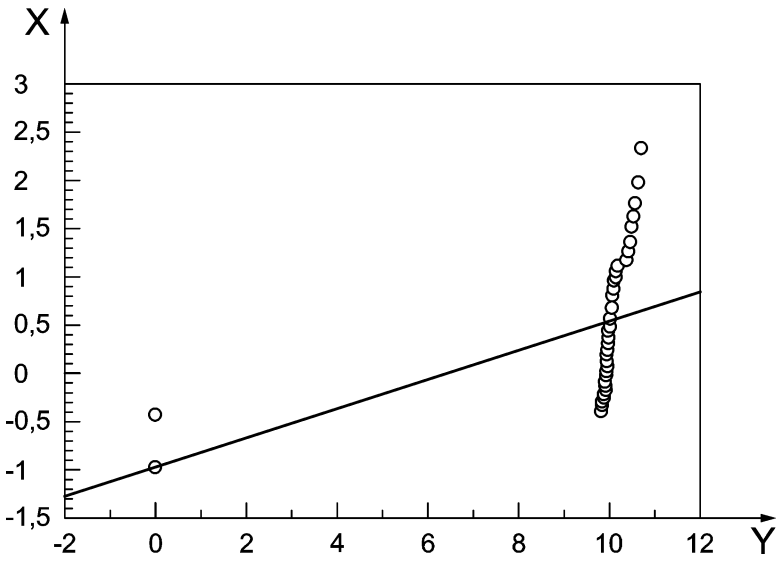
Key

X min

Y pA

1 i-Butanol

Figure 10 — Example of an i-butanol plot

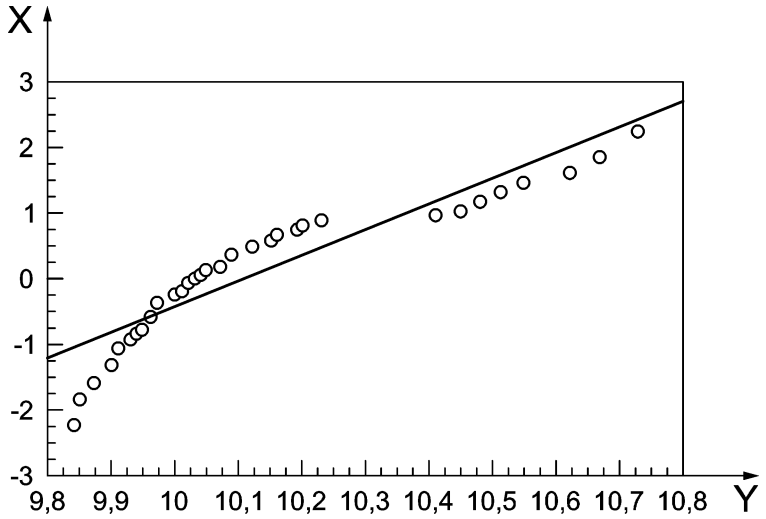


Key

X Expected Normal Value

Y i-Butanol content, % (*V/V*)

Figure 11 — Sample 4, n-Probability i-Butanol – all data



Key

X Expected Normal Value

Y i-Butanol content, % (*V/V*)

Figure 12 — Sample 4, n-Probability i-Butanol - unidentified removed

7 Results and conclusions

From the returned data an estimate of the precision is calculated (see Table 11). Laboratories that reported a value of zero were excluded from the calculations. Reprocessing with correct identification may have given a correct result.

Precision estimates have been calculated according to EN ISO 4259. These figures have been incorporated in EN ISO 22854.

Table 11 — Estimated precision data for oxygenates

Component	Concentration % (*V/V*)	Repeatability	Reproducibility	Valid laboratories
Methanol	3	0,24	3,8	35 (*)
t-Butanol	6,7	0,13	0,48	26
i-Propanol	10	0,19	1,35	26
i-Butanol	10,1	0,24	0,65	23
MTBE	0,25	0,05	0,13	22
MTBE	8,3	0,17	0,52	25
MTBE	11,5	0,2	0,8	32

Methanol: no data removed.

t-Butanol: laboratories removed = 6, 18, 19, 22, 24, 30, 32, 35 and 44.

i-Propanol: laboratories removed = 2, 17, 18, 19, 22, 24, 30, 32, 33, 35 and 44.

i-Butanol: laboratories removed = 11, 16, 17, 18, 22, 24, 25, 29, 30, 31, 32, 35 and 44.

The reproducibility of i-propanol is higher than for the other components, mainly because it can appear as a double peak and then both peaks have to be identified properly. The repeatability indicates that a better precision can be obtained when comparing the ratio reproducibility / repeatability with the ratio for i-butanol.

The reproducibility of Methanol is far greater than anticipated from the repeatability. The main cause is that Methanol is a fairly active component. When analysing this component one has to be careful with the proper operation of the precolumn.

The reproducibility of MTBE agrees with the precision stated in EN 14517.

There are more issues with oxygenated components that are not commonly found in production gasoline. The main issue is failing to identify a component properly, which causes 20 % to 30 % rejects. With identification issues removed the precision of the components is acceptable. When unknown oxygenates are found in a sample, the identification should be verified using a reference mixture or a mixture with added pure component.

Annex A
(normative)

Round Robin Report 2010 - 688

A.1 General

The Round Robin that this Annex addresses was organized by CEN/TC 19/WG 9 and held for the determination of Oxygenates in E85 Fuels.

A specific request was made by the E85 Task Force to look at the possibilities to establish a test method to determine oxygenated components in E85. The responsible working group CEN/TC 19/WG 9 selected four methods for evaluation:

— a modified EN ISO 22854 method with sample dilution,

— a modified EN 1601 method (O-FID) with sample dilution,

— a capillary column method with two columns in series (UNGDA method), and

— a capillary column method with two separate columns (Suedzucker method).

The results of this RR are given in this Annex.

A.2 Motivation

A.2.1 General

Target was to find out test method applicability in E85 and precision for the GC determination of oxygenates for the ethanol test methods A, B, C, D listed below.

— Method A EN ISO 22854 with dilution
— Method B EN 1601 with dilution
— Method C UNGDA Method (2 capillary columns in series)
— Method D Suedzucker Method (2 capillary columns, separated analysis)

For each of these test methods, results were sought for the following analyte groups

— Ethanol (RRT 2010 – 688 part 1)
— Benzene (RRT 2010 – 688 part 2)
— C3 to C5 alcohols (RRT 2010 – 688 part 3)
— Ethers (RRT 2010 – 688 part 4)

A.2.2 Remarks

Except for method A, test methods were not executed with a satisfactory number of laboratories. This means that a full RRT precision evaluation for methods B, C, D was not possible with the necessary significance. For these methods it was tried to conduct another RRT (2010-689), however again with not enough laboratories.

Therefore, results for methods B, C, and D are not conclusive, and only some statistical summary is given for these methods.

In addition, levels for the different analytes were not separately designed to keep the overall effort in control. This results in a somewhat uneven spacing of content level for some analytes. Therefore, transformations as described in EN ISO 4259 have not been applied.

A.3 Test Procedure and Protocol

A.3.1 General

Test method was EN ISO 22854 using a sample pre-dilution step (1 part sample with 4 parts dilutant).

A.3.2 Participating Laboratories Method A

14 Laboratories reported results for method A (Laboratories listed in alphabetical order)

— AC Analytical Controls BV

— Adam Opel GmbH

— ASG Analytik Service GmbH

— BP Gelsenkirchen

— CEPSA Research

— Conoco Phillips

— GMA mbH

— OMV Refining & Marketing GmbH

— Petroplus Raffinerie Ingolstadt

— PSA Peugeot-Citroen

— Repsol

— SGS Germany GmbH

— SGS Nederland BV

— Total CReG

A.3.3 Samples

10 samples with Ethanol content ranging from approximately 50 % to 85 % (*V/V*) have been used (see Figure A.1). For preparing the blends two different Ethanol samples and two petrol samples (without oxygenates) were used and blend in the order shown in Table A.1.

NOTE Samples were prepared by Petrolab.

Table A.1 — Sample Blending in % (*V/V*)

	Ethanol 1	Ethanol 2	BOB 1	BOB 2
S1	50	0	50	0
S2	55	0	0	45
S3	0	60	40	0
S4	0	65	0	35
S5	90	0	10	0
S6	0	87	0	13
S7	0	85	15	0
S8	83	0	0	17
S9	63	0	37	0
S10	0	70	0	30

The samples were analysed for the following groups:

— Ethanol content;

— Total ether content;

— Combined C3 to C5 alcohols content;

— Benzene content.

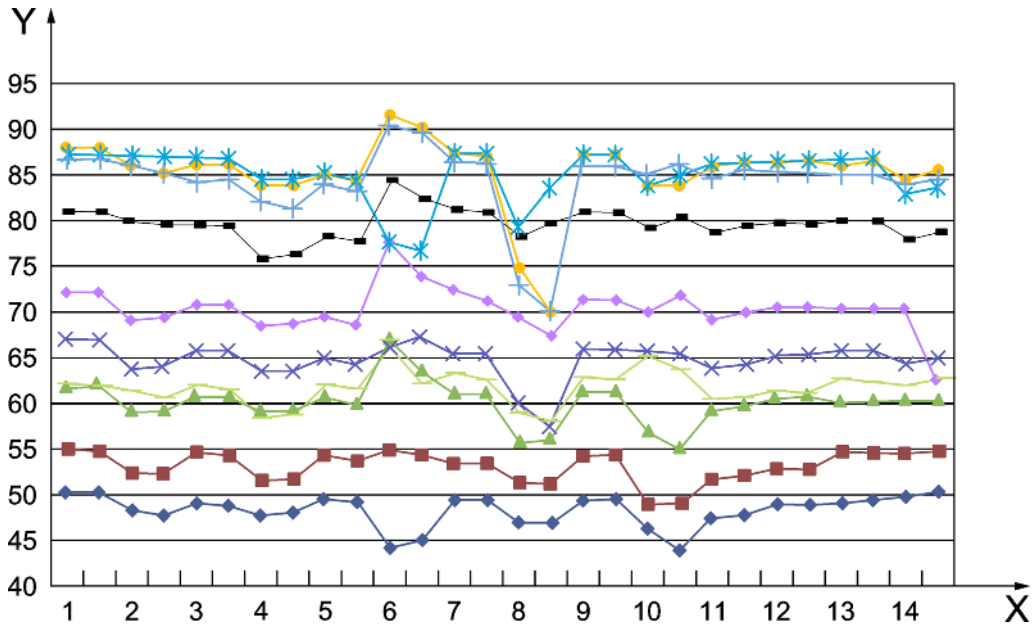
The results of the laboratory analyses and the precision evaluation for each group are given in A.3.4.

A.3.4 Results and Precision Evaluation

A.3.4.1 Results Method A – Ethanol

The Ethanol content in the samples ranged from approx. 50 % to 85 % (*V/V*). The laboratory results for Ethanol are shown in Table A.2 where only the raw data is shown.

Table A.3 contains the precision evaluation results which are shown in Figure A.2.



Key

X	Lab ID	S5	
Y	Ethanol content	S6	
S1		S7	
S2		S8	
S3		S9	
S4		S10	

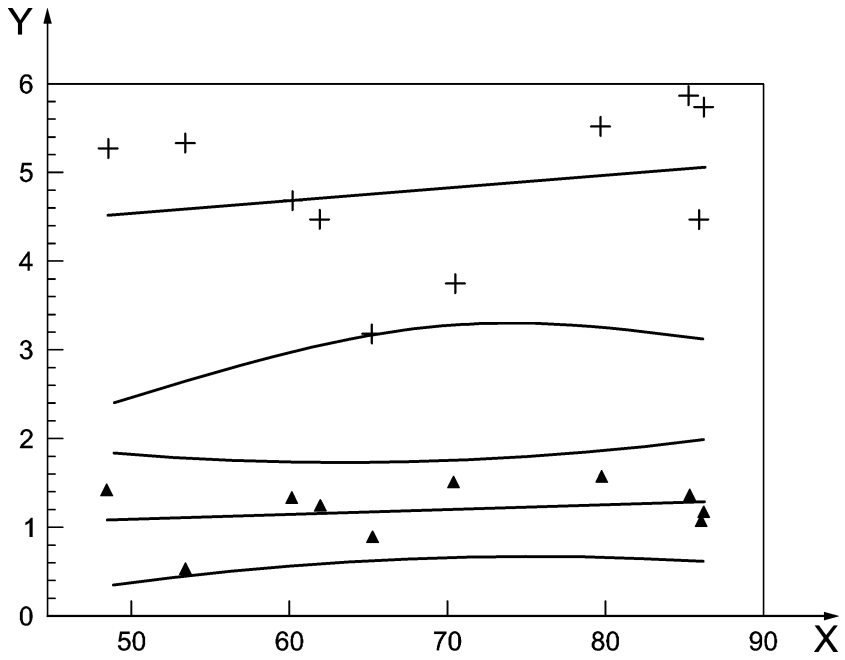
Figure A.1 — Results Method A - Ethanol – Lab-Sample Plot

Table A.2 — Results Method A - Ethanol – Laboratory Results

2010–688–1 RRT Ethanol Method A															
Lab		**Sample 1**			**Sample 2**			**Sample 3**			**Sample 4**			**Sample 5**	
1	+	50,21	50,30	+	55,06	54,92	+	61,75	62,10	+	67,01	66,83	+	87,24	87,33
2	+	48,42	47,83	+	52,40	52,39	+	59,13	59,14	+	63,87	64,13	+	87,03	87,01
3	+	49,04	48,91	+	54,87	54,48	+	60,80	60,89	+	65,69	65,76	+	86,86	86,94
4	+	47,90	48,01	+	51,66	51,72	+	59,21	59,37	+	63,61	63,42	+	84,57	84,48
5	+	49,42	49,28	+	54,30	53,78	+	60,86	60,06	+	65,08	64,35	+	85,34	84,50
6	+	44,57	45,06	+	55,03	54,56	C	66,97	63,63	+	66,17	67,29	H	77,58	76,69
7	+	49,39	49,41	+	53,47	53,52	+	61,02	61,04	+	65,48	65,40	+	87,35	87,50
8	H	47,05	47,07	H	51,43	51,22	H	55,81	56,25	H	60,24	57,38	H	79,28	83,56
9	+	49,32	49,55	+	54,40	54,41	+	61,37	61,26	+	66,03	65,96	+	87,44	87,28
10	+	46,26	44,10	+	48,97	49,11	+	57,05	55,21	+	65,76	65,38	+	83,49	84,84
11	+	47,44	47,85	+	51,82	52,20	+	59,30	59,87	+	64,03	64,29	+	86,32	86,57
12	+	48,95	48,95	+	52,86	52,75	+	60,68	60,83	+	65,32	65,33	+	86,35	86,42
13	+	49,04	49,42	+	54,72	54,67	+	60,07	60,31	+	65,74	65,88	+	86,86	86,99
14	+	49,86	50,29	+	54,55	54,72	+	60,16	60,28	+	64,38	64,81	+	82,94	83,60
Lab		**Sample 6**			**Sample 7**			**Sample 8**			**Sample 9**			**Sample 10**	
1	+	88,01	88,03	+	86,65	86,74	+	81,03	80,89	+	62,27	61,98	+	72,11	72,21
2	+	85,98	85,31	+	85,99	85,10	+	79,85	79,55	+	61,33	60,70	+	69,05	69,35
3	+	86,15	86,16	+	84,24	84,54	+	79,53	79,49	+	61,99	61,66	+	70,74	70,77
4	+	84,00	83,88	+	82,00	81,37	+	75,80	76,25	+	58,54	58,90	+	68,50	68,70
5	+	85,06	84,40	+	83,97	83,17	+	78,35	77,79	+	62,15	61,58	+	69,48	68,67
6	+	91,55	90,24	+	90,35	89,49	+	84,43	82,43	C	66,33	62,40	C	78,01	73,87
7	+	87,43	87,07	+	86,43	86,40	+	81,31	80,94	+	63,33	62,64	+	72,49	71,27
8	H	74,95	70,26	H	72,88	70,14	H	78,24	79,79	H	59,10	58,17	H	69,37	67,54
9	+	87,14	87,21	+	85,87	85,88	+	81,00	80,86	+	62,90	62,77	+	71,31	71,29
10	+	83,91	83,94	+	85,10	86,29	+	79,32	80,44	+	65,16	63,85	+	70,19	71,85
11	+	85,97	86,39	+	84,66	85,55	+	78,69	79,45	+	60,47	60,77	+	69,29	69,84
12	+	86,43	86,64	+	85,42	85,29	+	79,75	79,60	+	61,33	61,30	+	70,58	70,58
13	+	86,19	86,51	+	85,02	85,03	+	80,03	80,04	+	62,76	62,30	+	70,40	70,43
14	+	84,56	85,53	+	83,85	84,48	+	77,93	78,63	+	62,01	62,73	C	70,37	62,52

Table A.3 — Results Method A - Ethanol – Precision Results

	Reproducibility *R* = 3,8461 + 0,0144 × MV [% (*V/V*)] Repeatability *r* = 0,8488 + 0,0056 × MV [% (*V/V*)]				
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
(Nr. of Laboratories) Valid Laboratories	(14) 13	(14) 13	(14) 12	(14) 13	(14) 12
Mean Value MV	48,42	53,36	60,07	65,27	86,05
Repeatability *r*	1,450	0,561	1,352	0,920	1,111
Reproducibility *R*	5,288	5,350	4,691	3,208	4,499
Degrees of Freedom	13	12	12	13	12
Anderson Darling Criterium	0,898	0,733	0,64	0,201	0,817
	Sample 6	**Sample 7**	**Sample 8**	**Sample 9**	**Sample 10**
(Nr. of Laboratories) Valid Laboratories	(14) 13	(14) 13	(14) 13	(14) 12	(14) 11
Mean Value MV	86,30	85,34	79,75	61,89	70,41
Repeatability *r*	1,200	1,378	1,600	1,270	1,534
Reproducibility *R*	5,745	5,887	5,537	4,489	3,774
Degrees of Freedom	13	13	13	12	12
Anderson Darling Criterium	0,371	0,468	0,343	0,3	0,222



Key

X Mean in % (*V/V*)

Y Repeatability / Reproducibility

+ Reproducibility (*R*)

▲ Repeatability (*r*)

Figure A.2 — Repeatability and Reproducibility Plot

The round robin test result fulfils the “2R”–rule for the E85 Specification for ethanol. Constant precision values instead of formulas can be used due to the very small slopes of both repeatability and reproducibility.

r = 1, 238 % (*V*/*V*), to be rounded to adequate No of significant digits.

R = 4, 847 % (*V*/*V*), to be rounded to adequate No of significant digits.

A.3.4.2 Results Method A – Ethers

The Ethers content in the samples ranged from approx. 0,25 to 1,6 % (*V/V*). The laboratory results for Ethers are shown in Table A.4 where only the raw data is shown.

Table A.5 contains the precision evaluation results.

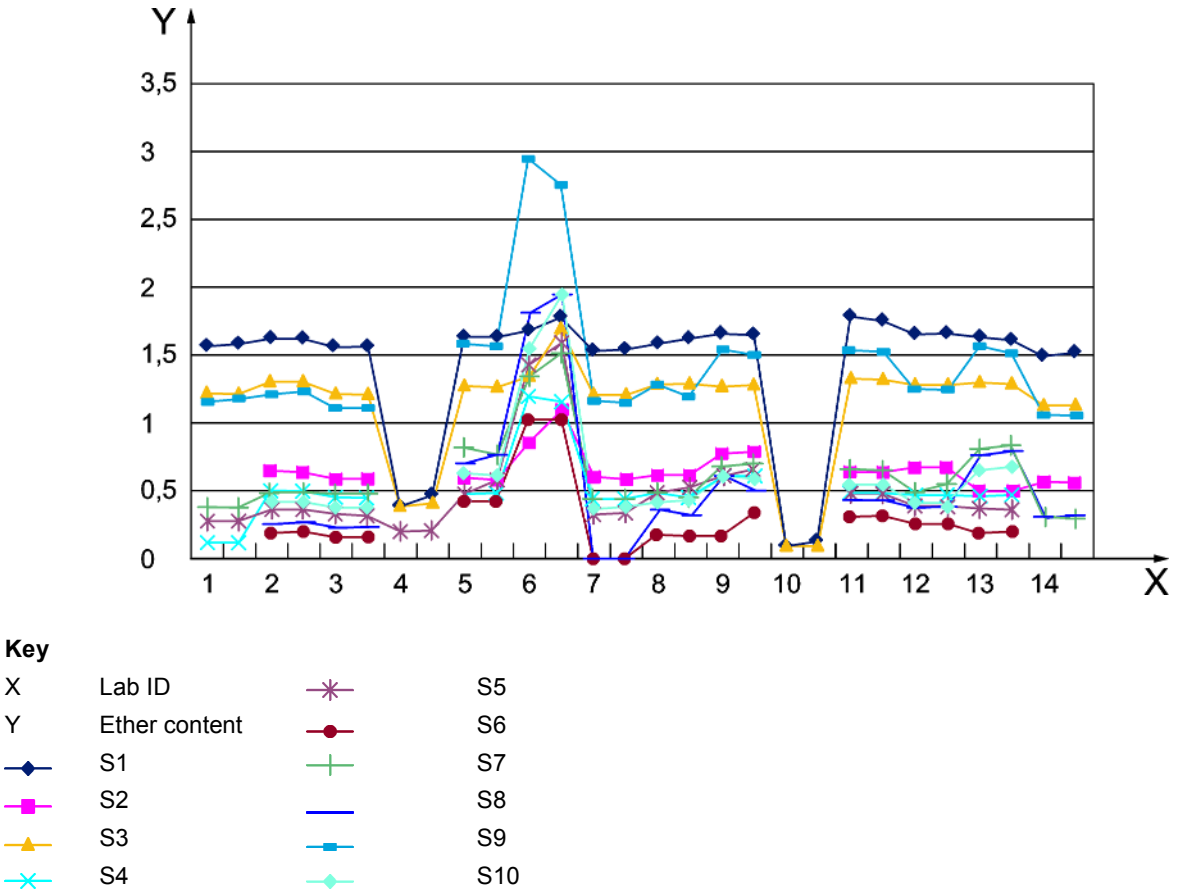


Figure A.3 — Results Method A - Ethers – Lab-Sample Plot

Table A.4 — Results Method A - Ethers – Laboratory Results

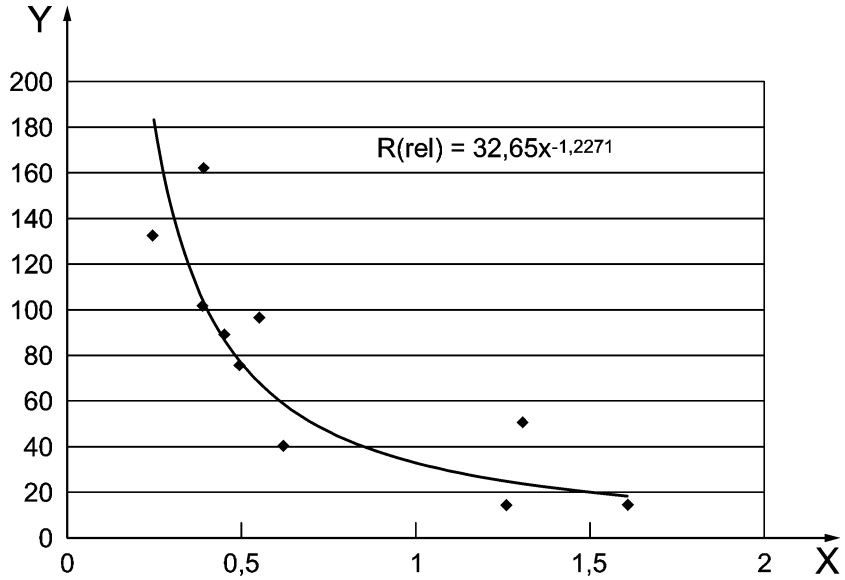
LAB		Sample 1			Sample 2			Sample 3			Sample 4			Sample 5	
1	+	1,57	1,58	+	0	0	+	1,23	1,22	+	0,12	0,12	+	0,28	0,28
2	+	1,62	1,62	+	0,65	0,64	+	1,31	1,31	+	0,50	0,50	+	0,37	0,36
3	+	1,56	1,56	+	0,59	0,59	+	1,22	1,22	+	0,45	0,45	+	0,33	0,32
4	H	0,41	0,46	+	0	0	H	0,40	0,42	+	0	0	+	0,20	0,21
5	+	1,63	1,63	+	0,60	0,59	+	1,28	1,27	+	0,48	0,48	C	0,47	0,58
6	C	1,68	1,77	C	0,85	1,08	C	1,36	1,7	H	1,20	1,16	C	1,43	1,59
7	+	1,53	1,54	+	0,60	0,59	+	1,21	1,21	+	0,45	0,45	+	0,33	0,33
8	+	1,58	1,62	+	0,62	0,61	+	1,29	1,3	+	0,47	0,45	+	0,49	0,52
9	+	1,66	1,65	+	0,78	0,79	+	1,28	1,29	+	0,61	0,61	+	0,61	0,66
10	H	0,11	0,12	+	0	0	H	0,11	0,1	+	0	0	+	0	0
11	+	1,78	1,75	+	0,64	0,64	+	1,34	1,33	+	0,49	0,49	+	0,48	0,48
12	+	1,66	1,66	+	0,67	0,67	+	1,28	1,28	+	0,47	0,47	+	0,39	0,39
13	+	1,63	1,61	+	0,49	0,49	+	1,31	1,3	+	0,46	0,47	+	0,37	0,36
14	+	1,49	1,51	+	0,57	0,56	+	1,14	1,14	+	0	0	+	0	0

LAB		Sample 6			Sample 7			Sample 8			Sample 9			Sample 10	
1	+	0	0	+	0,38	0,38	+	0	0	+	1,16	1,17	+	0	0
2	+	0,19	0,20	+	0,49	0,49	+	0,26	0,27	+	1,21	1,23	+	0,43	0,42
3	+	0,16	0,16	+	0,48	0,48	+	0,23	0,23	+	1,11	1,11	+	0,38	0,38
4	+	0	0	+	0	0	+	0	0	H	0	0	+	0	0
5	+	0,42	0,42	+	0,81	0,77	C	0,70	0,79	+	1,58	1,57	+	0,63	0,62
6	H	1,03	1,03	C	1,33	1,51	C	1,81	1,94	C	2,94	2,75	C	1,54	1,95
7	+	0	0	+	0,44	0,44	+	0	0	+	1,16	1,14	+	0,37	0,38
8	+	0,18	0,17	+	0,48	0,46	+	0,36	0,32	C	1,28	1,19	+	0,41	0,44
9	C	0,17	0,34	+	0,68	0,70	C	0,61	0,5	+	1,54	1,5	+	0,58	0,59
10	+	0	0	+	0	0	+	0	0	H	0	0	+	0	0
11	+	0,31	0,31	+	0,66	0,65	+	0,43	0,43	+	1,53	1,52	+	0,55	0,56
12	+	0,26	0,26	+	0,49	0,55	+	0,38	0,38	+	1,25	1,25	+	0,40	0,41
13	+	0,19	0,20	+	0,81	0,84	+	0,76	0,79	+	1,57	1,51	+	0,66	0,68
14	+	0	0	+	0,31	0,30	+	0,30	0,32	+	1,06	1,05	+	0	0

Table A.5 — Results Method A - Ethers – Precision Results

	Reproducibility R = 0,4544 + −0,0795 × MV [% (V/V)]				
	Repeatability r = 0,0297 + 0,0062 × MV [% (V/V)]				
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
(Nr. of Laboratories) Valid Laboratories	(14) 11	(14) 10	(14) 11	(14) 10	(14) 10
Mean Value MV	1,61	0,62	1,26	0,45	0,39
Repeatability r	0,040	0,017	0,016	0,016	0,044
Reproducibility R	0,226	0,245	0,180	0,399	0,395
Degrees of Freedom	10	9	10	9	9
Anderson Darling Criterium	0,243	0,404	0,433	1,528	0,292
	Sample 6	**Sample 7**	**Sample 8**	**Sample 9**	**Sample 10**
(Nr. of Laboratories) Valid Laboratories	(14) 7	(14) 11	(14) 7	(14) 10	(14) 9
Mean Value MV	0,25	0,55	0,39	1,31	0,49
Repeatability r	0,015	0,056	0,049	0,056	0,033
Reproducibility R	0,323	0,530	0,634	0,655	0,375

Degrees of Freedom	6	10	6	9	8
Anderson Darling Criterium	0,474	0,359	0,655	0,705	0,559



Key

X Ether content, % (*V/V*)

Y Rel. Reproducibility, *R* (in % of X)

Figure A.4 — Relative Reproducibility Plot

Remarks:

— The E85 Specification for Ethers is max 7,7 %(*V/V*). The Round Robin only covered ethers in the range of approx. 0,25 % to 1,6 % (*V/V*) (Several laboratories did not report values but entered a “0” if components were not identified (these values were treated as not reported);

— “2*R* – rule not fulfilled for X < ~ 0,5 %(*V/V*) (Advise is to use a constant value for *R* at X > ~0,5).

r = 0,0342 % (V/V) to be rounded to adequate No of significant digits.

R = 0,326 % (V/V) to be rounded to adequate No of significant digits.

A.3.4.3 Results Method A – C3 to C5 Alcohols

The C3 to C5 alcohol content ranged from approx. 1,4 % to 2,5 % (*V/V*). The laboratory results for C3 to C5 alcohols are shown in Table A.6 where only the raw data is shown.

Table A.7 contains the precision evaluation results

Samples 3, 4, 6, 7 and 10 did not contain any C3-C5 alcohols.

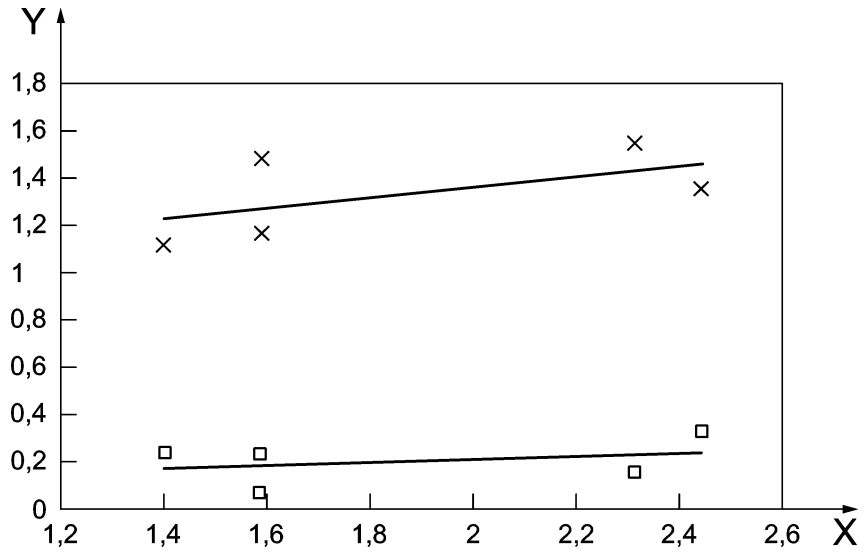
Table A.6 — Results Method A - C3 to C5 Alcohols – Laboratory Results

Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
1	1	1,46	1,68	0	0	2,68	0	0	2,44	1,88	0
	2	1,47	1,68	0	0	2,70	0	0	2,46	1,89	0
2	1	1,07	1,20	0	0	2,11	0	0	1,95	1,38	0
	2	1,10	1,21	0	0	2,10	0	0	1,92	1,43	0
3	1	0,96	1,31	0	0	2,21	0	0	1,95	1,45	0
	2	0,96	1,31	0	0	2,19	0	0	1,93	1,46	0
4	1	1,97	2,07	0,53	0,56	2,13	0,27	0,39	2,38	2,19	0,48
	2	1,94	2,05	0,53	0,56	2,09	0,27	0,38	2,37	2,27	0,44
5	1	1,07	1,22	0	0	2,17	0	0	1,89	1,38	0
	2	1,09	1,20	0	0	2,13	0	0	1,88	1,36	0
6	1	2,06	2,52	0	0	2,52	0	0	3,23	2,07	0
	2	1,92	2,40	0	0	2,81	0	0	3,12	1,86	0
7	1	1,27	1,00	0	0	2,04	0	0	1,53	1,22	0
	2	0,96	0,68	0	0	1,63	0	0	1,53	1,20	0
8	1	1,67	1,80	0	0	3,07	0	0	3,22	2,24	0
	2	1,48	1,65	0	0	3,36	0	0	3,00	1,84	0
9	1	1,16	1,26	0	0	2,03	0	0	1,86	1,42	0
	2	1,14	1,25	0	0	2,05	0	0	1,86	1,42	0
10	1	1,71	1,97	0,78	0,10	2,08	0	0	2,08	1,43	0
	2	2,23	2,02	1,06	0	2,14	0	0	1,94	1,49	0
11	1	1,50	1,63	0	0	2,84	0	0	2,53	1,88	0
	2	1,52	1,64	0	0	2,83	0	0	2,54	1,88	0
12	1	1,78	1,91	0	0	3,21	0	0	2,89	2,22	0
	2	1,75	2,05	0	0	3,20	0	0	2,92	2,22	0
13	1	1,17	1,27	0	0	2,31	0	0	2,05	1,42	0
	2	1,17	1,28	0	0	2,27	0	0	2,05	1,44	0
14	1	0,33	0,35	0	0	2,71	0	0	2,56	1,09	0
	2	0,33	0,35	0	0	2,71	0	0	2,57	1,07	0

The precision results for C3 to C5 alcohols are shown in Table A.7 and Figure A.5.

Table A.7 — Results Method A - C3 to C5 Alcohols – Precision Results

	Reproducibility *R* = 0,0731 + 0,6963 × MV [% (*V/V*)]				
	Repeatability *r* = 0,0011 + 0,1032 × MV [% (*V/V*)]				
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
(Nr. of Laboratories) Valid Laboratories	14/12	(14) 13	(14) 12	(14) 12	(14) 14
Mean Value MV	1,40	1,59	-	-	2,44
Repeatability *r*	0,248	0,242	-	-	0,337
Reproducibility *R*	1,125	1,481	-	-	1,361
Degrees of Freedom	12	12	n. def.	n. def.	14
Anderson Darling Criterium	0,538	0,342	n. def.	n. def.	0,657
	Sample 6	**Sample 7**	**Sample 8**	**Sample 9**	**Sample 10**
(Nr. of Laboratories) Valid Laboratories	(14) 13	(14) 13	(14) 14	(14) 12	(14) 12
Mean Value MV	-	-	2,31	1,59	-
Repeatability *r*	-	-	0,165	0,075	-
Reproducibility *R*	-	-	1,546	1,171	-
Degrees of Freedom	n. def.	n. def.	13	11	n. def.
Anderson Darling Criterium	n. def.	n. def.	0,429	0,742	n. def.



Key

X Mean

Y Repeatability / Reproducibility

Figure A.5 — Precision Plots Method A for C3 to C5 Alcohols

Remarks:

— The E85 Spec for C3 to C5 alcohols is max 6,0 %(*V*/*V*). The Round Robin only covers these alcohols in the range of 1,4 % to 2,5 %(*V*/*V*)

— Only 5 of the 10 samples contained C3 to C5 Alcohols. There were no samples close to the limit of 6,0 %(*V*/*V*)The "2*R*" – rule is barely fulfilled at levels near 2 %(*V*/*V*). It might work for higher levels, but no significant proof is obtained from this RRT.

Conclusion: data should be interpreted only with extreme scepticism.

A.3.4.4 Results Method A - Benzene

The Benzene content in the samples ranged from approx. 0,1 % to 0,5 % (*V*/*V*). The laboratory results for benzene are shown in Table A.8 where only the raw data is shown.

Table A.9 contains the precision evaluation results

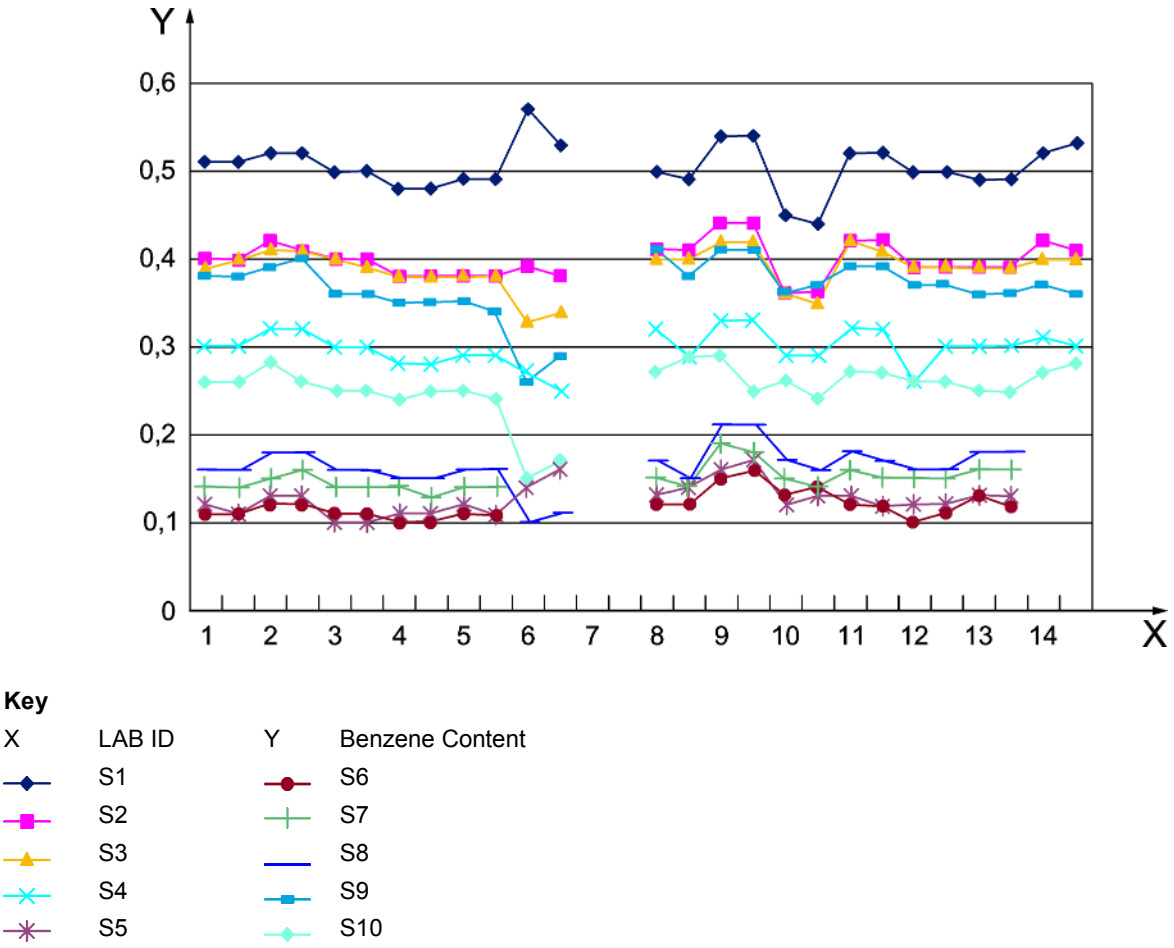


Figure A.6 — Results Method A - Benzene – Lab-Sample Plot

The laboratory results for benzene (2010-688-2 RRT Benzene Method A) are shown in Table A.8

Table A.8 — Results Method A - Benzene – Laboratory Results

LAB		Sample 1			Sample 2			Sample 3			Sample 4			Sample 5	
1	+	0,51	0,51	+	0,4	0,4	+	0,39	0,40	+	0,3	0,3	+	0,12	0,11
2	+	0,52	0,52	+	0,42	0,41	+	0,41	0,41	+	0,32	0,32	+	0,13	0,13
3	+	0,50	0,50	+	0,4	0,4	+	0,40	0,39	+	0,3	0,3	+	0,10	0,10
4	+	0,48	0,48	+	0,38	0,38	+	0,38	0,38	+	0,28	0,28	+	0,11	0,11
5	+	0,49	0,49	+	0,38	0,38	+	0,38	0,38	+	0,29	0,29	+	0,12	0,11
6	+	0,57	0,53	+	0,39	0,38	+	0,33	0,34	+	0,27	0,25	+	0,14	0,16
7	x	-	-	x	-	-	x	-	-	x	-	-	x	-	-
8	+	0,50	0,49	+	0,41	0,41	+	0,40	0,40	+	0,32	0,29	+	0,13	0,14
9	+	0,54	0,54	+	0,44	0,44	+	0,42	0,42	+	0,33	0,33	+	0,16	0,17
10	+	0,45	0,44	+	0,36	0,36	+	0,36	0,35	+	0,29	0,29	+	0,12	0,13
11	+	0,52	0,52	+	0,42	0,42	+	0,42	0,41	+	0,32	0,32	+	0,13	0,12

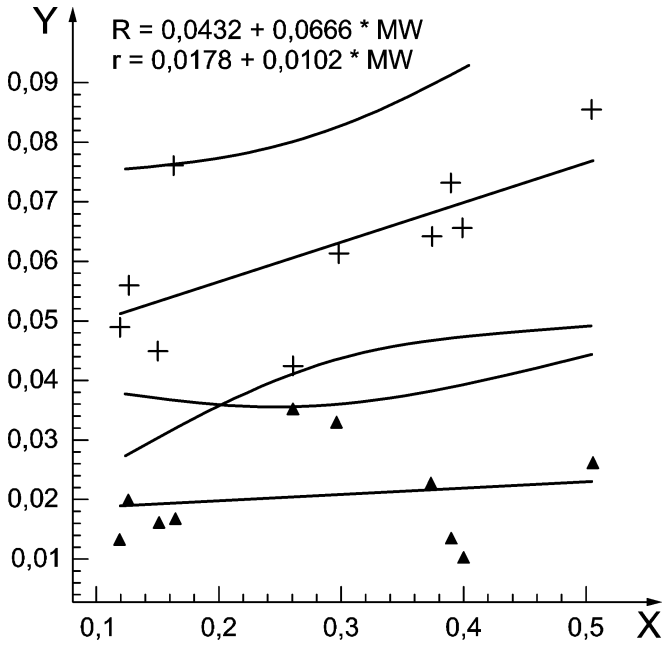
12	+	0,50	0,50	+	0,39	0,39	+	0,39	0,39	+	0,26	0,3	+	0,12	0,12
13	+	0,49	0,49	+	0,39	0,39	+	0,39	0,39	+	0,3	0,3	+	0,13	0,13
14	+	0,52	0,53	+	0,42	0,41	+	0,40	0,40	+	0,31	0,3	x	-	-
LAB		**Sample 6**			**Sample 7**			**Sample 8**			**Sample 9**			**Sample 10**	
1	+	0,11	0,11	+	0,14	0,14	+	0,16	0,16	+	0,38	0,38	+	0,26	0,26
2	+	0,12	0,12	+	0,15	0,16	+	0,18	0,18	+	0,39	0,40	+	0,28	0,26
3	+	0,11	0,11	+	0,14	0,14	+	0,16	0,16	+	0,36	0,36	+	0,25	0,25
4	+	0,10	0,10	+	0,14	0,13	+	0,15	0,15	+	0,35	0,35	+	0,24	0,25
5	+	0,11	0,11	+	0,14	0,14	+	0,16	0,16	+	0,35	0,34	+	0,25	0,24
6	x	< 0,1	< 0,1	x	< 0,1	< 0,1	+	0,10	0,11	H	0,26	0,29	H	0,15	0,17
7	x	-	-	x	-	-	x	-	-	x	-	-	x	-	-
8	+	0,12	0,12	+	0,15	0,14	+	0,17	0,15	+	0,41	0,38	+	0,27	0,29
9	+	0,15	0,16	+	0,19	0,18	+	0,21	0,21	+	0,41	0,41	+	0,29	0,25
10	+	0,13	0,14	+	0,15	0,14	+	0,17	0,16	+	0,36	0,37	+	0,26	0,24
11	+	0,12	0,12	+	0,16	0,15	+	0,18	0,17	+	0,39	0,39	+	0,27	0,27
12	+	0,10	0,11	+	0,15	0,15	+	0,16	0,16	+	0,37	0,37	+	0,26	0,26
13	+	0,13	0,12	+	0,16	0,16	+	0,18	0,18	+	0,36	0,36	+	0,25	0,25
14	x	-	-	x	-	-	x	-	-	+	0,37	0,36	+	0,27	0,28

The precision results for benzene are shown in Table A.9 and Figure A.7.

Table A.9 — Results Method A - Benzene – Precision Results

	Reproducibility R = 0,0432 + 0,0666 × MV [% (m/m)]				
	Repeatability r = 0,0178 + 0,0102 × MV [% (m/m)]				
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
(Nr. of Laboratories) Valid Laboratories	(13) 13	(13) 13	(13) 13	(13) 13	(12) 12
Mean Value MV	0,51	0,40	0,39	0,30	0,13
Repeatability r	0,026	0,010	0,013	0,033	0,020
Reproducibility R	0,085	0,066	0,073	0,061	0,056
Degrees of Freedom	13	12	12	16	12
Anderson Darling Criterium	0,231	0,196	0,51	0,256	0,33
	Sample 6	**Sample 7**	**Sample 8**	**Sample 9**	**Sample 10**
(Nr. of	(12) 11	(12) 11	(12) 12	(13) 12	(13) 12

Laboratories) Valid Laboratories					
Mean Value MV	0,12	0,15	0,16	0,37	0,26
Repeatability *r*	0,013	0,016	0,017	0,023	0,035
Reproducibility *R*	0,049	0,045	0,076	0,064	0,042
Degrees of Freedom	11	11	12	12	19
Anderson Darling Criterium	0,502	0,651	0,839	0,307	0,514



Key

X Mean in % (*m*/*m*)

Y Repeatability / Reproducibility

+ Reproducibility (*R*)

▲ Repeatability (*r*)

Figure A.7 — Precision Plots Method A for Benzene

Remarks:

— The “2*R*” rule is fulfilled for all samples;

— the Benzene determination is currently not part of the E85 spec.

*r = 0,0178 + 0,0102 * X* to be rounded to adequate No of significant digits.

*R = 0,0432 + 0,0666 * X* to be rounded to adequate No of significant digits.

A.4 Essential RRT Details Methods B, C, D

A.4.1 Test Procedure and Protocol

Test method was EN ISO 22854 using a sample pre-dilution step (1 part sample with 4 parts dilutant).

A.4.2 Participating Laboratories Method B, C and D

— Biocarburantes de Castilla y León, S.A.

— Eidgenössische Alkoholverwaltung (EAV)

— GMA mbH

— PSA Peugeot-Citroen

— Repsol

— SGS Germany GmbH

— Suedzucker AG

→ No estimators and no interpretation is given

→ For these methods an overview is given on the next slides

A.4.3 Samples

For methods B, C, D, the same sample set as for method A was used: 10 samples with Ethanol content ranging from approx. 50 % to 85 % (*V/V*) (see Table A.10).

Samples were prepared by Petrolab.

Table A.10 — Sample Blending in %(*V/V*)

	Ethanol 1	Ethanol 2	BOB 1	BOB2
S1	50	0	50	0
S2	55	0	0	45
S3	0	60	40	0
S4	0	65	0	35
S5	90	0	10	0
S6	0	87	0	13
S7	0	85	15	0
S8	83	0	0	17
S9	63	0	37	0
S10	0	70	0	30

The Essential RRT Details for Ethanol using Methods B, C, D are shown in Table A.11.

Table A.11 — Essential RRT Details - Ethanol Methods B, C, D

Method B - EN 1601											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
1	1	46,74	52,01	59,33	64,35	83,81	86,57	84,55	77,76	59,63	68,59
	2	46,87	52,01	59,92	65,18	83,73	86,78	84,02	77,90	59,46	68,75
2	1	47,85	53,23	60,52	65,59	86,41	82,27	85,78	79,59	60,48	69,11
	2	47,75	53,06	59,01	64,77	88,27	82,71	84,96	79,25	60,18	69,42
8	1	46,71	52,65	59,83	65,78	86,18	88,43	85,37	80,75	60,60	70,71
	2	47,21	53,19	60,13	66,32	88,03	89,01	86,89	81,33	61,65	71,41
Method C - UNGDA											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
15	1	49,19	45,28	60,03	66,65	79,56	80,13	78	72,39	55,28	71,98
	2	49,21	45,28	60,13	66,51	79,65	80,41	77,87	72,51	55,54	71,94
Method D - Suedzucker											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
15	1	46,63	51,10	58,53	63,95	85,47	86,26	84,37	77,93	58,78	68,73
	2	46,48	51,21	59,03	63,81	84,95	86,58	83,69	78,57	58,93	69,17
16	1	47,60	51,20	57,70	64,10	87,00	86,00	85,20	80,30	60,10	69,70
	2	46,70	50,90	57,30	63,40	86,30	85,60	84,30	79,60	59,60	69,60
17	1	47,33	51,94	59,49	65,27	88,68	89,07	87,74	80,71	59,75	68,73
	2	46,64	50,00	57,83	64,00	87,28	87,98	86,35	80,11	57,69	69,91
6	1	45,92	50,89	57,78	63,31	85,32	86,00	85,11	78,85	59,05	69,25
	2	45,73	50,60	58,17	63,41	84,92	87,69	85,21	78,85	59,74	70,33

The Essential RRT Details for Ethers using Methods B, C, D are shown in Table A.12.

Table A.12 — Essential RRT Details - Ethers Methods B, C, D

Method B - EN 1601											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
1	1	1,78	0,46	1,28	0,36	0,50	0,21	0,56	0,18	1,24	0,33
	2	1,76	0,46	1,17	0,36	0,48	0,22	0,50	0,19	1,18	0,34
2	1	0,00	0,60	0,00	0,63	0,00	0,28	0,00	0,71	0,00	0,62
	2	0,00	0,45	0,00	0,27	0,00	0,20	0,00	1,15	0,00	0,59
8	1	1,44	0,53	1,00	0,00	0,00	0,00	0,00	0,00	1,01	0,00
	2	1,43	0,56	1,04	0,00	0,00	0,00	0,00	0,00	1,03	0,00
Method C - UNGDA											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
15	1	1,80	0,02	1,43	0,13	0,35	0,04	0,49	0,02	1,23	0,11
	2	1,80	0,02	1,43	0,13	0,35	0,04	0,49	0,02	1,24	0,11
Method D - Suedzucker											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
15	1										
	2										
16	1										
	2										
17	1	1,71	0,64	1,34	0,48	0,37	0,18	0,49	0,27	1,27	0,41
	2	1,70	0,65	1,34	0,48	0,37	0,18	0,49	0,28	1,28	0,42
6	1	1,63	0,44	1,29	0,36	0,35	0,16	0,48	0,20	1,22	0,33
	2	1,63	0,39	1,30	0,35	0,35	0,16	0,49	0,21	1,22	0,32

The Essential RRT Details for C3 to C5 alcohols using Methods B, C, D are shown in Table A.13.

Table A.13 — Essential RRT Details - C3 to C5 Alcohols Methods B, C, D

Method B - EN 1601											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
1	1										
	2										
2	1	0	0	0	0	0	0	0	0	0	0
	2	0	0	0	0	0	0	0	0	0	0
8	1	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5
	2	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5
Method C - UNGDA											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
15	1	5,43	3,29	3,72	4,74	2,8	1,81	1,67	2,74	4,23	4,13
	2	5,43	3,29	3,72	4,74	2,8	1,81	1,68	2,74	4,2	4,13
Method D - Suedzucker											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
15	1										
	2										
16	1	0,91	1,01	0	0	1,75	0	0	1,69	1,59	0
	2	0,99	1,09	0	0	1,84	0	0	1,69	1,68	0
17	1	1,26	1,28	0,11	0,11	2,06	0,04	0,04	1,89	1,45	0,09
	2	1,23	1,29	0,10	0,11	2,07	0,04	0,04	1,88	1,53	0,10
6	1	0,97	1,02	0,11	0,12	1,26	0,03	0,00	1,22	1,20	0,09
	2	0,95	1,01	0,08	0,10	1,33	0,03	0,00	1,20	1,17	0,11

The Essential RRT Details for benzene using Method D are shown in Table A.14.

Table A.14 — Essential RRT Details - Benzene Method D

Method D - Suedzucker											
Results											
Lab		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
16	1	0,43	0,36	0,31	0,24	0,11	0,09	0,11	0,15	0,34	0,21
	2	0,45	0,35	0,30	0,23	0,10	0,08	0,11	0,15	0,33	0,20
17	1	0,49	0,37	0,38	0,28	0,12	0,11	0,14	0,16	0,35	0,24
	2	0,51	0,38	0,40	0,30	0,12	0,11	0,15	0,17	0,39	0,26

The Essential RRT Details for methanol using Methods B, C, D are shown in Table A.15.

Table A.15 — Essential RRT Details - Methanol Methods B, C, D

Method B - EN 1601											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
2	1	0	0	0	0	0	0	0	0	0	0
	2	0	0	0	0	0	0	0	0	0	0
8	1	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5
	2	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5
Method C - UNGDA											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
15	1	0,15	0,14	0,15	-	0,21	-	0,04	0,2	0,16	-
	2	0,14	0,14	0,15	-	0,2	-	0,04	0,19	0,15	-
Method D - Suedzucker											
Results											
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
16	1	0,10	0,11	0	0	0,18	0	0	0,17	0,17	0
	2	0,10	0,12	0	0	0,19	0	0	0,17	0,17	0
17	1	0,16	0,17	< 0,001	< 0,001	0,28	< 0,001	< 0,001	0,24	0,21	< 0,001
	2	0,16	0,15	< 0,001	< 0,001	0,27	< 0,001	< 0,001	0,23	0,21	< 0,001

Annex B
(normative)

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B.1 Methods and laboratories used

The Round Robin was organized by CEN/TC 19/WG 9 and a 2nd Round Robin held for the determination of Oxygenates in E85 Fuels.

An additional, small scale, Round Robin was conducted to get more data for methods B, C and D as only a limited number of laboratories provided data for these methods in the first Round Robin. This RR was held in the December 2010 - January 2011 timeframe.

Method A was run as well for comparison.

2nd Round Robin held for the determination of Oxygenates in E85 Fuels. Following methods were examined

A EN ISO 22854 (with sample dilution)

B EN 1601 (with sample dilution)

C UNGDA-method

D Suedzucker-method

The participating laboratories are shown in Table B.1.

Table B.1 — Participating Laboratories (in alphabetical order)

AC Analytical Controls BV	Netherlands
ASG Analytik Service GmbH	Germany
Biocarburantes de Castilla y León, S.A.	Spain
BP Europe SE - Global Fuels Technology	Germany
CEPSA Centro de Investigacion	Spain
Cristal Union	France
Eidgenössische Alkoholverwaltung EAV	Switzerland
GMA mbH	Germany
Interscience B.V.	Netherlands
SGS Germany GmbH	Germany
Suedzucker AG	Germany
Tereos BENP	France
UNGDA	France

B.2 Samples

The samples were prepared by Petrolab using two different kinds of ethanol that were blended with a base EN 228 gasoline according to the scheme presented in Table B.2 (all values approximately and in %*(V/V)*).

The base gasoline contained app. 5 % (*V/V*) ETBE.

Table B.2 — Sample Blending in %(*V/V*)

Sample	Ethanol A	Ethanol B	EN 228	Methanol
1	X	–	40	0,2
2	–	X	35	0,2
3	X	–	30	0,5
4	–	X	25	0,5
5	X	–	20	0,8
6	–	X	15	0,8

B.3 Results received

B.3.1 General

Each participant received a protocol for the method they were running and a result sheet to fill in the data. Duplicate results were requested.

An overview of all results is given in Tables B.4, B.5, B.6 and B.7. The ethanol results are also shown graphically in Figures B.1 and B.2.

The results required were related to the CEN/TS 15293 spec for E85:

— Ethanol

— Ethers (Total)

— C3 to C5 Alcohols

— Methanol

— Benzene

The samples contained hardly any higher alcohols, so no results were reported for C3 to C5 Alcohols.

B.3.2 Conclusions

As was seen in the first RR, it was very hard to get enough participants for method B, C and D, and when results were reported, not all laboratories were able to provide data for all groups.

Table B.3 — Overview of the number of participants per method

	Method A	Method B	Method C	Method D
Ethanol	5	4	5	4
Ethers	5	2	4	3
Methanol	4	2	5	3
Benzene	5	-	3	3

For method A the results showed a better performance for ethanol and ethers compared to the first RR and confirmed the applicability of the method for these groups.

The data received for method B, C and D showed quite some deviations between the laboratories and it was not possible to evaluate the precision for them.

Three laboratories reported additional components for method C, not mentioned in the result sheet, such as iso-pentanol, acetaldehyde and ethyl acetate.

B.3.3 Overview results received

Table B.4 — Method A

Ethanol							
Lab	**Repeat**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**
5	1	61,58	65,85	72	76,03	77,72	83,09
	2	62,05	66,4	72,13	76,27	77,85	82,85
6	1	61,6	66,81	71,48	76,69	79,65	84,17
	2	62,07	66,56	71,19	76,4	79,24	84,2
7	1	60,06	65,52	69,83	75,81	80,02	86,1
	2	59,23	64,33	69,59	76,08	79,59	86,13
9	1	60,51	66,31	68,59	72,28	77,85	83,45
	2	59,76	63,68	68,8	74,34	76,38	81,86
11	1	62,87	67,66	71,9	77,24	80,24	85,78
	2	62,29	67,45	71,79	77,38	79,63	85,75
Mean		61,20	66,06	70,73	75,85	78,82	84,34
Stdev		1,22	1,27	1,38	1,51	1,27	1,53
Min		59,23	63,68	68,59	72,28	76,38	81,86
Max		62,87	67,66	72,13	77,38	80,24	86,13

Ethers							
Lab	**Repeat**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**
5	1	2,13	1,97	1,5	1,3	1	0,73
	2	2,12	1,92	1,5	1,28	1	0,72
6	1	2,04	1,96	1,58	1,36	1,15	0,92
	2	2,09	2,02	1,61	1,38	1,16	0,92
7	1	2,13	1,97	1,7	1,52	1,06	0,96
	2	2,14	2,08	1,61	1,36	1,27	0,79
9	1	2,19	2,03	1,75	1,52	1,21	0,92
	2	2,26	2,14	1,73	1,49	1,18	1
11	1	2,05	1,76	1,38	1,19	1,02	1,01
	2	2,05	1,75	1,38	1,18	1,21	1
Mean		2,12	1,96	1,57	1,36	1,13	0,90
Stdev		0,07	0,13	0,13	0,12	0,10	0,11
Methanol							
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
5	1				0,79	0,9	1,24
	2				0,85	0,91	1,28
6	1				0,33	0,36	0,49
	2				0,35	0,37	0,5
9	1	0,34	0,42	0,47	0,68	0,71	1,03
	2	0,28	0,47	0,58	0,76	0,77	0,97
11	1	0,39	0,5	0,71	0,71	0,71	1,04
	2	0,38	0,51	0,79	0,76	0,76	1,1
Mean		0,35	0,48	0,64	0,65	0,69	0,96
Stdev		0,05	0,04	0,14	0,20	0,21	0,30
Benzene							
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6

5	1	0,43	0,37	0,3	0,24	0,21	0,14
	2	0,43	0,37	0,3	0,24	0,2	0,14
6	1	0,51	0,44	0,37	0,29	0,25	0,19
	2	0,49	0,42	0,36	0,29	0,25	0,19
7	1	0,47	0,4	0,35	0,28	0,23	0,17
	2	0,46	0,41	0,35	0,28	0,23	0,17
9	1	0,46	0,4	0,31	0,3	0,23	0,18
	2	0,48	0,42	0,37	0,3	0,26	0,2
11	1	0,41	0,36	0,3	0,25	0,22	0,14
	2	0,41	0,36	0,3	0,24	0,22	0,14
Mean		0,46	0,40	0,33	0,27	0,23	0,17
Stdev		0,03	0,03	0,03	0,03	0,02	0,02

Table B.5 — Method B

Ethanol							
Lab	**Repeat**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**
2	1	68,30	74,00	78,50	82,50	81,20	81,30
	2	69,80	72,90	76,90	82,30	80,50	80,90
7	1	62,54	65,16	71,54	76,36	81,29	86,77
	2	62,68	66,33	71,04	77,38	83,00	87,10
9	1	61,18	65,78	70,83	75,24	79,26	85,92
	2	60,77	66,30	70,69	76,82	79,67	85,51
10	1	61,92	66,84	71,71	77,10	85,96	80,74
	2	62,30	66,68	71,68	77,12	86,17	80,55
Mean		63,69	68,00	72,86	78,10	82,13	83,60
Stdev		3,40	3,42	3,04	2,73	2,68	2,96
Min		60,77	65,16	70,69	75,24	79,26	80,55
Max		69,80	74,00	78,50	82,50	86,17	87,10

Ethers							
Lab	**Repeat**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**
9	1	1,65	1,51	1,13	0,90	0,67	
	2	1,68	1,55	1,13	0,90	0,66	
10	1	1,94	1,84	1,45	1,19	0,68	0,94
	2	1,94	1,80	1,42	1,19	0,68	0,94
Mean		1,80	1,68	1,28	1,04	0,67	0,94
Stdev		0,16	0,17	0,18	0,17	0,01	0,00
Methanol							
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
9	1	0,00	0,00	0,00	0,55	0,55	0,97
	2	0,00	0,00	0,00	0,55	0,54	0,96
10	1	0,14	0,17	0,46	0,74	1,13	0,76
	2	0,14	0,22	0,50	0,82	1,23	0,80
Mean		0,07	0,10	0,24	0,66	0,86	0,87
Stdev		0,08	0,11	0,28	0,14	0,37	0,11

Table B.6 — Method C

Ethanol							
Lab	**Repeat**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**
1	1	60,30	65,33	72,49	76,52	77,20	88,10
	2	63,05	65,48	69,45	78,80	78,31	86,14
3	1	66,02	69,33	76,56	80,44	83,14	89,10
	2	65,98	69,33	76,48	80,47	83,30	89,11
12	1	58,25	68,86	75,21	71,64	85,80	77,96
	2	56,92	68,86	73,86	70,84	85,91	78,34
8	1	63,53	68,10	73,04	79,01	81,71	86,11
	2	63,31	67,40	71,81	77,83	81,20	86,53

13	1	59,38	56,89	62,88	66,28	70,23	77,34
	2	59,50	57,49	63,86	66,81	71,33	78,68
Mean		61,62	65,71	71,56	74,86	79,81	83,74
Stdev		3,19	4,72	4,83	5,50	5,53	5,00
Min		56,92	56,89	62,88	66,28	70,23	77,34
Max		66,02	69,33	76,56	80,47	85,91	89,11
Ethers							
Lab	**Repeat**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**
1	1	3,55	3,33	2,67	2,16	1,68	1,57
	2	3,55	3,34	2,67	2,16	1,69	1,57
3	1	1,85	1,70	1,42	1,26	0,96	0,92
	2	1,86	1,69	1,49	1,17	0,96	0,87
8	1	2,17	2,02	1,59	1,34	1,06	0,76
	2	2,19	2,03	1,59	1,33	1,06	0,76
13	1	2,24	1,84	1,51	1,22	0,97	0,74
	2	2,20	1,83	1,47	1,22	0,96	0,72
Mean		2,45	2,22	1,80	1,48	1,17	0,99
Stdev		0,70	0,70	0,54	0,42	0,32	0,36
Methanol							
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
1	1			0,54	0,90	0,91	1,30
	2			0,54	0,88	0,90	1,32
3	1	0,45	0,42	0,74	0,96	0,97	1,32
	2	0,45	0,41	0,74	0,96	0,98	1,33
8	1	0,20	0,21	0,50	0,78	0,80	1,17
	2	0,20	0,21	0,49	0,77	0,79	1,18
12	1	7,39	7,90	6,81	4,90	4,96	3,61
	2	7,37	7,90	6,72	4,97	4,92	3,61

13	1	3,79	2,85	2,68	2,25	2,14	2,03
	2	3,79	2,84	2,83	2,48	2,12	2,14
Mean		2,96	2,84	2,26	1,99	1,95	1,90
Stdev		3,12	3,31	2,54	1,67	1,66	0,96
Benzene							
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
1	1	0,45	0,42	0,34	0,27	0,22	0,19
	2	0,45	0,41	0,34	0,27	0,21	0,19
12	1	0,38	0,37	0,32	0,22	0,19	0,13
	2	0,37	0,34	0,31	0,22	0,20	0,13
13	1	0,40	0,32	0,28	0,21	0,18	0,12
	2	0,39	0,31	0,27	0,21	0,18	0,12
Mean		0,41	0,36	0,31	0,23	0,20	0,15
Stdev		0,04	0,04	0,03	0,03	0,02	0,03

Table B.7 — Method D

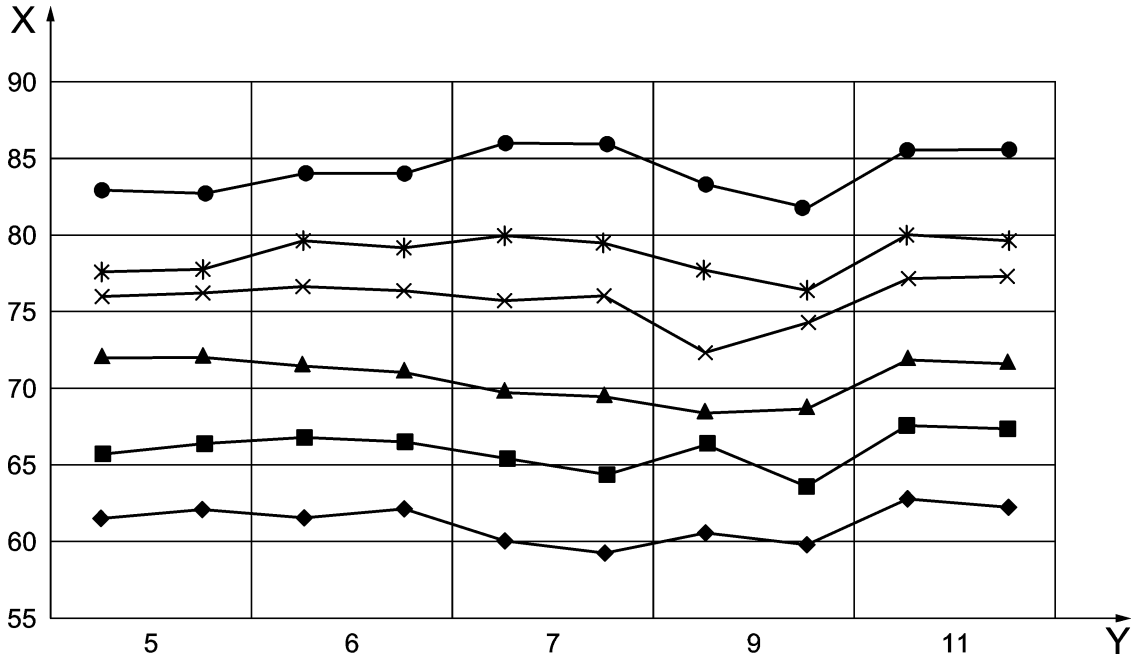
Ethanol							
Lab	**Repeat**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**
1	1	73,34	78,71	81,05	83,58	86,21	88,16
	2	71,51	78,90	81,21	84,91	83,50	86,82
3	1	64,46	68,57	72,77	77,74	81,36	86,68
	2	65,14	68,06	71,90	78,45	80,90	86,18
4	1	60,70	66,00	70,30	76,00	79,40	85,10
	2	60,10	65,30	70,40	76,10	79,90	84,90
8	1	59,46	65,63	70,99	76,70	80,31	85,83
	2	60,50	64,71	70,66	77,51	80,82	85,82
Mean		64,40	69,49	73,66	78,87	81,55	86,19
Stdev		5,38	5,90	4,68	3,44	2,25	1,05

Min		59,46	64,71	70,30	76,00	79,40	84,90
Max		73,34	78,90	81,21	84,91	86,21	88,16
Ethers							
Lab	**Repeat**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**
1	1	3,41	3,19	2,55	2,04	1,64	1,30
	2	3,39	3,18	2,54	2,04	1,64	1,30
4	1	2,02	1,87	1,49	1,25	0,99	0,72
	2	2,06	1,91	1,51	1,26	1,00	0,73
8	1	1,87	1,76	1,44	1,21	0,98	0,73
	2	1,87	1,78	1,43	1,24	0,96	0,76
Mean		2,44	2,28	1,83	1,51	1,20	0,92
Stdev		0,75	0,70	0,56	0,41	0,34	0,29
Methanol							
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
1	1	0,00	0,00	0,60	0,91	0,93	1,34
	2	0,00	0,00	0,59	0,90	0,97	1,33
4	1	0,36	0,36	0,81	1,25	1,27	1,87
	2	0,34	0,34	0,76	1,16	1,21	1,73
8	1	0,21	0,20	0,47	0,75	0,74	1,11
	2	0,21	0,20	0,48	0,73	0,72	1,16
Mean		0,19	0,18	0,62	0,95	0,97	1,42
Stdev		0,16	0,16	0,14	0,21	0,23	0,31
Benzene							
Lab	Repeat	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
1	1	0,46	0,42	0,34	0,27	0,22	0,17
	2	0,46	0,42	0,34	0,27	0,23	0,17
4	1	0,46	0,40	0,34	0,27	0,23	0,16
	2	0,46	0,40	0,34	0,26	0,23	0,15

8	1	0,39	0,35	0,30	0,25	0,21	0,84
	2	0,39	0,35	0,30	0,25	0,20	0,87
Mean		0,44	0,39	0,33	0,26	0,22	0,39
Stdev		0,04	0,03	0,02	0,01	0,01	0,36

B.4 Graphs

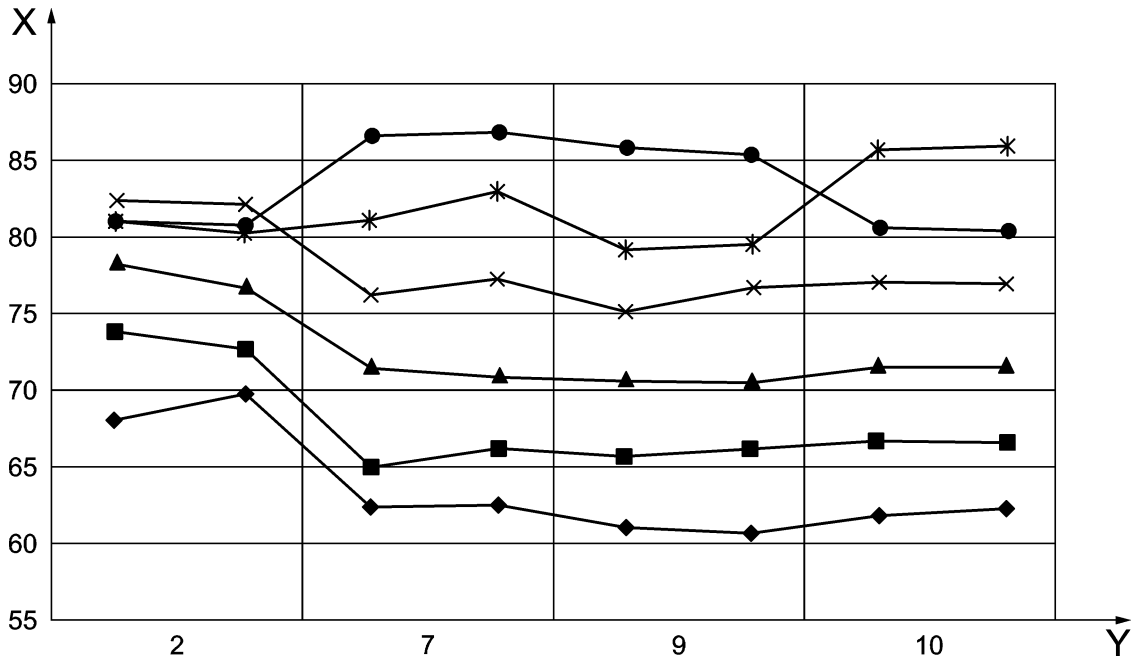
Figure B.1 shows % *V/V* Ethanol versus Lab no. per method:



Key

X	% *V/V* EtOH	▲	3
Y	Lab	×	4
◆	1	✳	5
■	2	●	6

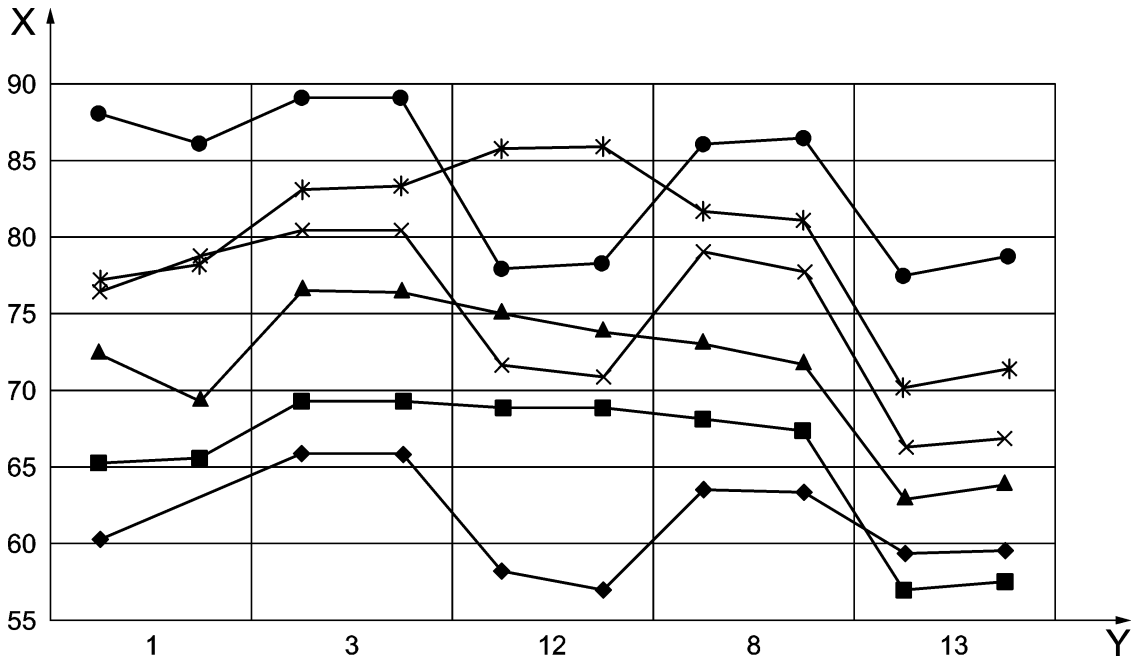
Figure B.1 — Method A E85 RR2



Key

X	% *V*/*V* EtOH	▲	3
Y	Lab	×	4
◆	1	✳	5
■	2	●	6

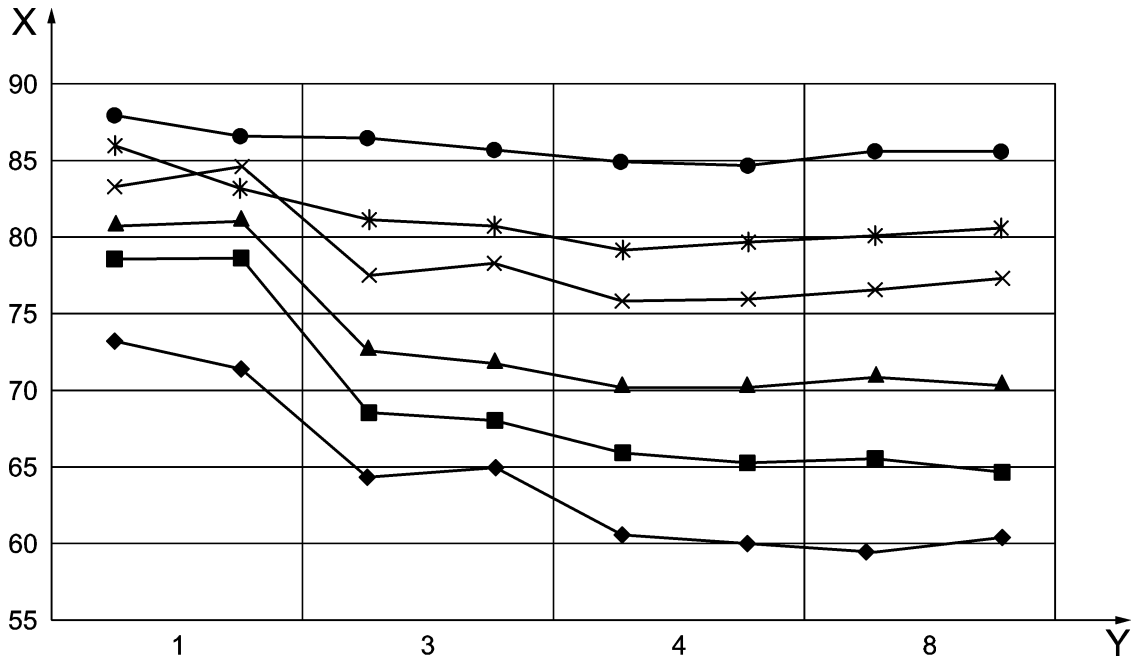
Figure B.2 — Method B E85 RR2



Key

X	% *V*/*V* EtOH	3	
Y	Lab	4	
1		5	
2		6	

Figure B.3 — Method C E85 RR2



Key

X	% *V*/*V* EtOH	3	
Y	Lab	4	
1		5	
2		6	

Figure B.4 — Method D E85 RR2

Bibliography

[1] EN 228, *Automotive fuels — Unleaded petrol — Requirements and test methods*

[2] EN 14517:2004, *Liquid petroleum products — Determination of hydrocarbon types and oxygenates in petrol — Multidimensional gas chromatography method*

[3] EN ISO 22854, *Liquid petroleum products — Determination of hydrocarbon types and oxygenates in automotive-motor gasoline and in ethanol (E85) automotive fuel — Multidimensional gas chromatography method (ISO 22854)*

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