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Tekoči naftni proizvodi - Določevanje vrste ogljikovodikov in oksigenatov z multidimenzionalno plinsko kromatografsko metodo - Medlaboratorijsko primerjalno poročilo

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 composés oxygénés par méthode par chromatrographie multidimensionnelle en phase gazeuse - Rapport de recherches interlaboratoires

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RAPPORT TECHNIQUE

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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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CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

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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.

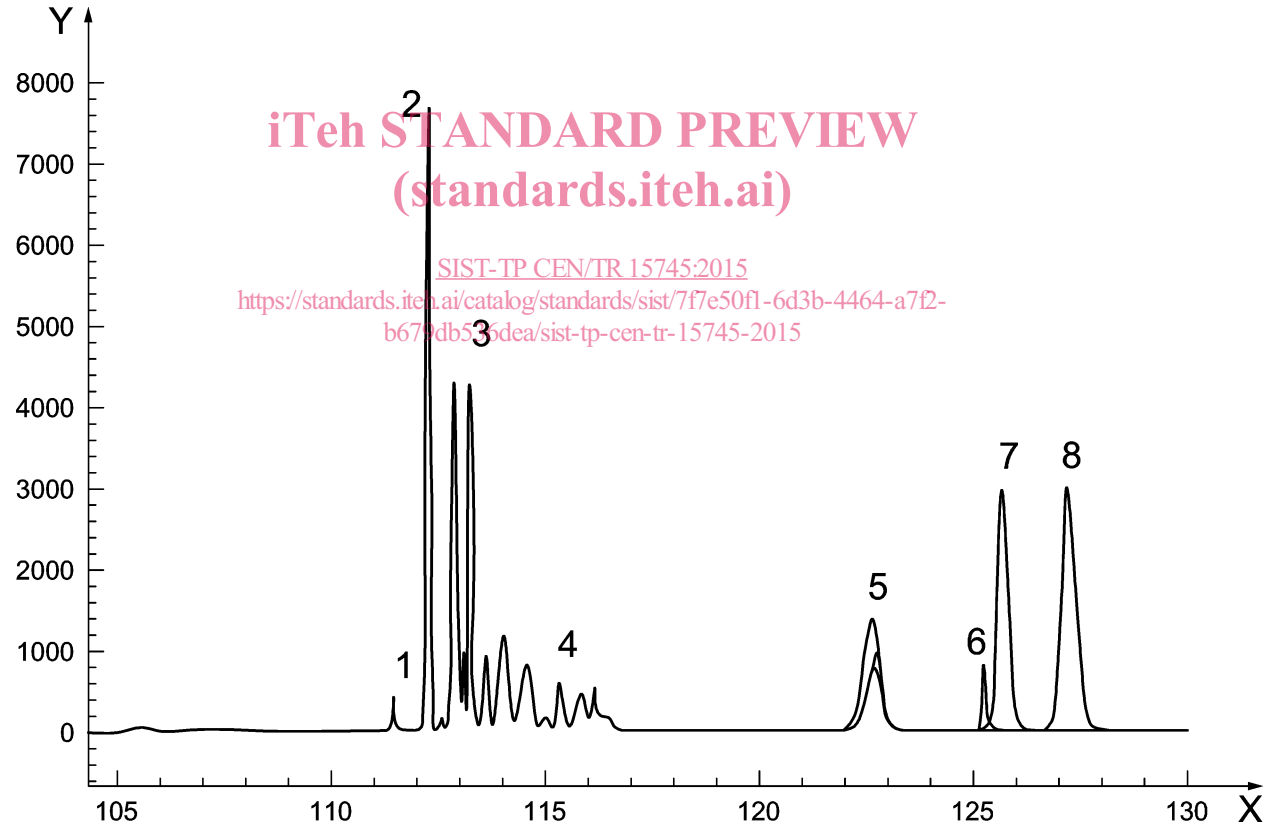
4 Sample set

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