Round-robin tests for

in-house measuring laboratories

Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA)
Institute for Occupational Safety and Health of the German Social Accident Insurance

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Results and evaluation

Organic solvents 2015

IFA
Institut für Arbeitsschutz der
Deutschen Gesetzlichen Unfallversicherung

Summary of laboratory means

Sample 1

	Ethyl acetate	Z score	n-Heptane	Z score	Toluene	Z score	m-Xylene	Z score
Unit	mg/tube		mg/tube		mg/tube		mg/tube	
6	0,275	-0,71	0,793	8,83 BE	0,438	0,40	0,126	0,19
10	0,288	-0,27	0,446	0,59	0,437	0,37	0,147	1,88
31	0,287	-0,30	0,364	-1,36	0,395	-0,62	0,114	-0,78
68	0,266	-1,01	0,393	-0,67	0,390	-0,74	0,114	-0,78
79			0,417	-0,10	0,431	0,22	0,127	0,23
82	0,322	0,88	0,448	0,64	0,414	-0,17	0,115	-0,70
85					0,440	0,45	0,140	1,32
100	0,301	0,17	0,394	-0,65	0,409	-0,29	0,122	-0,14
108	0,298	0,07	0,416	-0,12	0,423	0,04	0,130	0,51
114	0,325	0,98	0,442	0,49	0,457	0,85	0,131	0,59
118	0,304	0,27	0,393	-0,67	0,402	-0,46	0,120	-0,30
138	0,140	-5,27 BE	0,360	-1,45	0,280	-3,35 BE	0,180	4,55 BE
156	0,306	0,34	0,409	-0,29	0,421	-0,01	0,133	0,75
162	0,266	-1,01	0,408	-0,31	0,395	-0,62	0,114	-0,78
167	0,335	1,32	0,463	0,99	0,415	-0,15	0,120	-0,30
190	0,260	-1,21	0,350	-1,69	0,370	-1,22	0,101	-1,83
195	0,299	0,10	0,518	2,30 E	0,491	1,66	0,138	1,16
197					0,462	0,97	0,142	1,48
199	0,298	0,07	0,455	0,80	0,473	1,23	0,117	-0,54
208	0,304	0,27	0,407	-0,34	0,404	-0,41	0,122	-0,14
224	0,297	0,04	0,498	1,82	0,388	-0,79	0,115	-0,70
278					0,391	-0,72	0,110	-1,11
–	–	––	–	––	–	––	–	––
Method	ISO 5725-2		ISO 5725-2		ISO 5725-2		ISO 5725-2	
Assessment	|Z|<=2,00		|Z|<=2,00		|Z|<=2,00		|Z|<=2,00	
Mean	0,296		0,421		0,421		0,124	
Reproducibility s.d.	0,021		0,045		0,031		0,012	

	Ethyl acetate	Z score	n-Heptane	Z score	Toluene	Z score	m-Xylene	Z score
Rel. reproducibility s.d.	7,06 %		10,76 %		7,39 %		9,49 %	
Assigned value	0,296		0,421		0,421		0,124	
Reference value	0,301		0,411		0,420		0,123	
Target s.d.	0,030		0,042		0,042		0,012	
Rel. target s.d.:	10,00 %		10,00 %		10,00 %		10,00 %	
Lower limit of tolerance	0,237		0,337		0,337		0,099	
Upper limit of tolerance	0,355		0,505		0,505		0,148	
Type B outliers	1		1		1		1	
Type E outliers	1		2		1		1	
No. of laboratories that submitted results	18		19		22		22	
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	17		18		21		21	
Explanation of outlier types								
A: Single outlier	Grubbs							
B: Differing laboratory mean	Grubbs							
C: Excessive laboratory s.d.	Cochran							
D: Excluded manually								
E: mean outside tolerance limits								
F: |Score|>3,5								

Summary of laboratory means

Sample 2

	i-Butyl acetate	Z score		n-Butyl acetate	Z score		o-Xylene	Z score	
Unit	mg/tube			mg/tube			mg/tube		
6	0,357	-0,19		0,106	5,17	BE	0,084	0,59	
10	0,434	1,93	B	0,081	1,65		0,086	0,84	
31	0,372	0,22		0,068	-0,27		0,072	-0,93	
68	0,362	-0,05		0,066	-0,55		0,077	-0,30	
79							0,084	0,61	
82	0,387	0,63		0,068	-0,27		0,072	-0,93	
85							0,090	1,34	
100	0,363	-0,03		0,077	1,02		0,081	0,21	
108	0,372	0,22		0,079	1,23		0,080	0,09	
114	0,355	-0,25		0,064	-0,84		0,076	-0,42	
118	0,400	0,99		0,078	1,16		0,081	0,21	
138	0,260	-2,86	BE	0,090	2,88	E	0,120	5,12	BE
156	0,378	0,39		0,071	0,16		0,082	0,33	
162	0,351	-0,36		0,064	-0,84		0,072	-0,93	
167	0,379	0,41		0,072	0,30		0,082	0,33	
190	0,340	-0,66		0,057	-1,84		0,063	-2,06	E
195	0,357	-0,19		0,054	-2,27	E	0,093	1,72	
197							0,090	1,34	
199	0,328	-0,99		0,063	-0,98		0,078	-0,17	
208	0,371	0,19		0,072	0,30		0,080	0,08	
224	0,351	-0,36		0,064	-0,84		0,073	-0,80	
278							0,070	-1,18	
–	–	– –		–	– –		–	– –	
Method	ISO 5725-2			ISO 5725-2			ISO 5725-2		
Assessment	|Z|<=2,00			|Z|<=2,00			|Z|<=2,00		
Mean	0,364			0,070			0,079		
Reproducibility s.d.	0,018			0,009			0,007		

	i-Butyl acetate	Z score	n-Butyl acetate	Z score	o-Xylene	Z score
Rel. reproducibility s.d.	4,92 %		13,05 %		9,34 %	
Assigned value	0,364		0,070		0,079	
Reference value	0,377		0,071		0,081	
Target s.d.	0,036		0,007		0,008	
Rel. target s.d.:	10,00 %		10,00 %		10,00 %	
Lower limit of tolerance	0,291		0,056		0,063	
Upper limit of tolerance	0,437		0,084		0,095	
Type B outliers	2		1		1	
Type E outliers	1		3		2	
No. of laboratories that submitted results	18		18		22	
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	16		17		21	
Explanation of outlier types						
A: Single outlier	Grubbs					
B: Differing laboratory mean	Grubbs					
C: Excessive laboratory s.d.	Cochran					
D: Excluded manually						
E: mean outside tolerance limits						
F: |Score|>3,5						

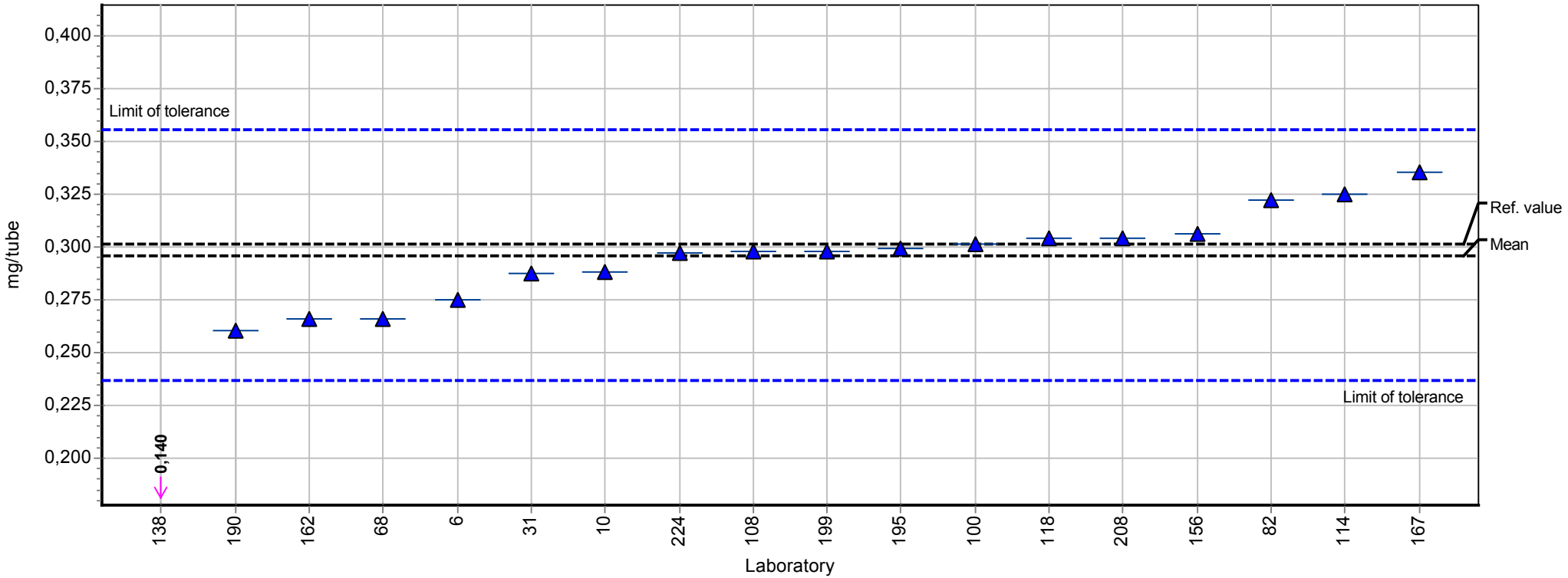
Summary of laboratory means

Sample 3

	n-Heptane	Z score	n-Hexane	Z score	n-Octane	Z score
Unit	mg/tube		mg/tube		mg/tube	
6	1,311	24,58 BE	0,704	0,36	0,642	8,20 BE
10	0,417	1,00	0,733	0,79	0,379	0,74
31	0,349	-0,80	0,616	-0,93	0,308	-1,27
68	0,356	-0,61	0,622	-0,85	0,336	-0,48
79	0,376	-0,09	0,586	-1,38	0,371	0,53
82	0,391	0,31	0,716	0,54	0,347	-0,16
85			0,580	-1,46		
100	0,358	-0,56	0,632	-0,70	0,339	-0,39
108	0,361	-0,48	0,689	0,14	0,345	-0,22
114	0,372	-0,19	0,698	0,27	0,341	-0,33
118	0,360	-0,50	0,637	-0,62	0,340	-0,36
138	0,290	-2,35 E	0,780	1,48	0,140	-6,03 BE
156	0,363	-0,43	0,632	-0,70	0,347	-0,16
162	0,365	-0,37	0,638	-0,61	0,342	-0,31
167	0,416	0,97	0,676	-0,05	0,345	-0,22
190	0,310	-1,82	0,540	-2,05 E	0,290	-1,78
195	0,487	2,84 E	0,876	2,89 E	0,418	1,85
199	0,439	1,58	0,849	2,50 E	0,383	0,86
208	0,363	-0,43	0,637	-0,62	0,336	-0,48
224	0,452	1,92	0,748	1,01	0,430	2,19 E
–	–	– –	–	– –	–	– –
Method	ISO 5725-2		ISO 5725-2		ISO 5725-2	
Assessment	|Z|<=2,00		|Z|<=2,00		|Z|<=2,00	
Mean	0,379		0,679		0,353	
Reproducibility s.d.	0,048		0,087		0,035	
Rel. reproducibility s.d.	12,72 %		12,76 %		9,89 %	
Assigned value	0,379		0,679		0,353	
Reference value	0,359		0,630		0,339	
Target s.d.	0,038		0,068		0,035	
Rel. target s.d.:	10,00 %		10,00 %		10,00 %	
Lower limit of tolerance	0,303		0,544		0,282	
Upper limit of tolerance	0,455		0,815		0,423	
Type B outliers	1				2	
Type E outliers	3		3		3	
No. of laboratories that submitted results	19		20		19	
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	18		20		17	
Explanation of outlier types						
A: Single outlier	Grubbs					
B: Differing laboratory mean	Grubbs					
C: Excessive laboratory s.d.	Cochran					
D: Excluded manually						
E: mean outside tolerance limits						
F: |Score|>3,5						

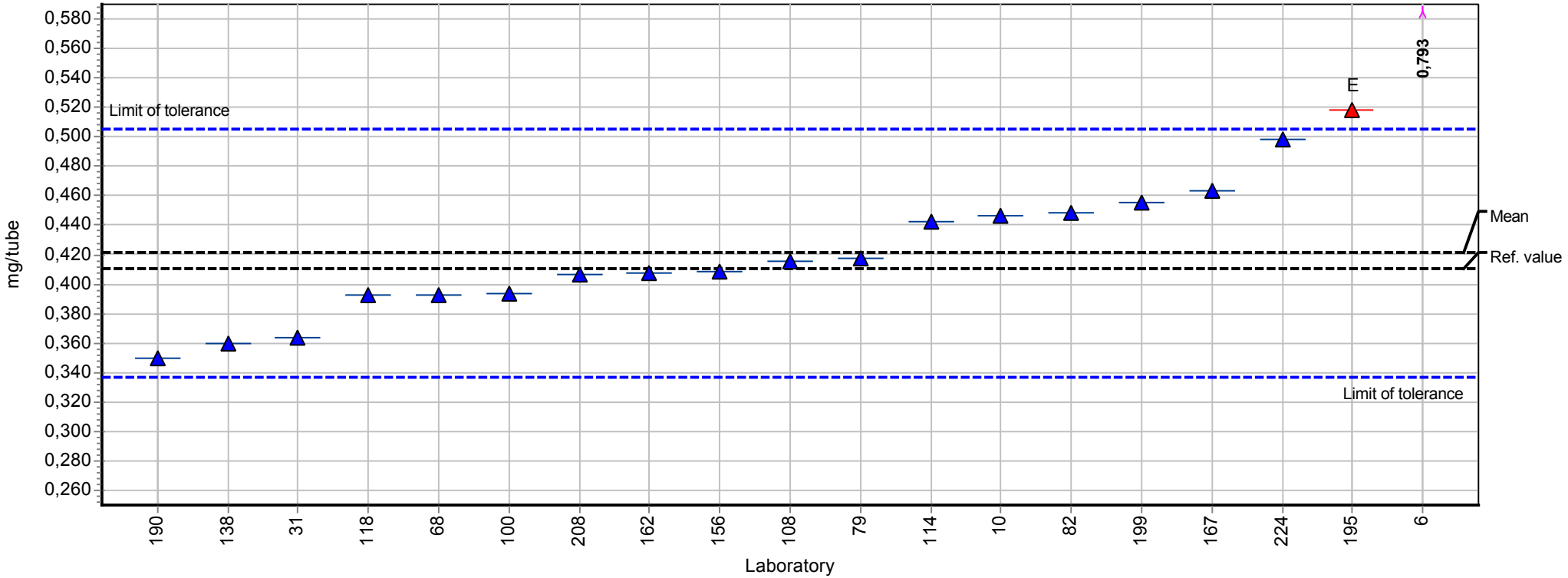
Summary results

Measurand:	**Ethyl acetate**	**Mean:**	**0,296 mg/tube**
Sample:	**1**	**Reproducibility s.d.:**	**0,021 mg/tube**
Method:	**ISO 5725-2**	**Relative reproducibility s.d.:**	**7,06%**
No. of laboratories:	**17**	**Reference value:**	**0,301 mg/tube**
Relative target s.d.:	**10,00% (Limited)**	**Range of tolerance:**	**0,237 - 0,355 mg/tube (|Z-Score| <= 2,00)**



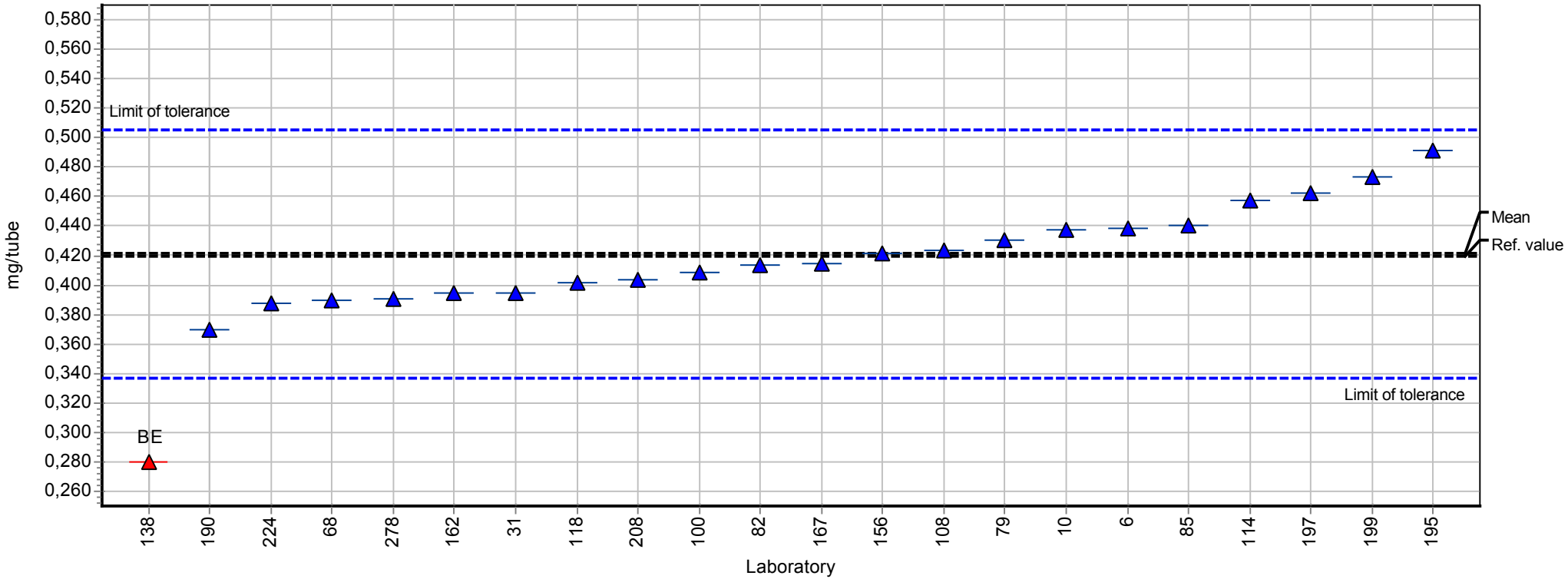
Summary results

Measurand:	**n-Heptane**	**Mean:**	**0,421 mg/tube**
Sample:	**1**	**Reproducibility s.d.:**	**0,045 mg/tube**
Method:	**ISO 5725-2**	**Relative reproducibility s.d.:**	**10,76%**
No. of laboratories:	**18**	**Reference value:**	**0,411 mg/tube**
Relative target s.d.:	**10,00% (Limited)**	**Range of tolerance:**	**0,337 - 0,505 mg/tube (|Z-Score| <= 2,00)**



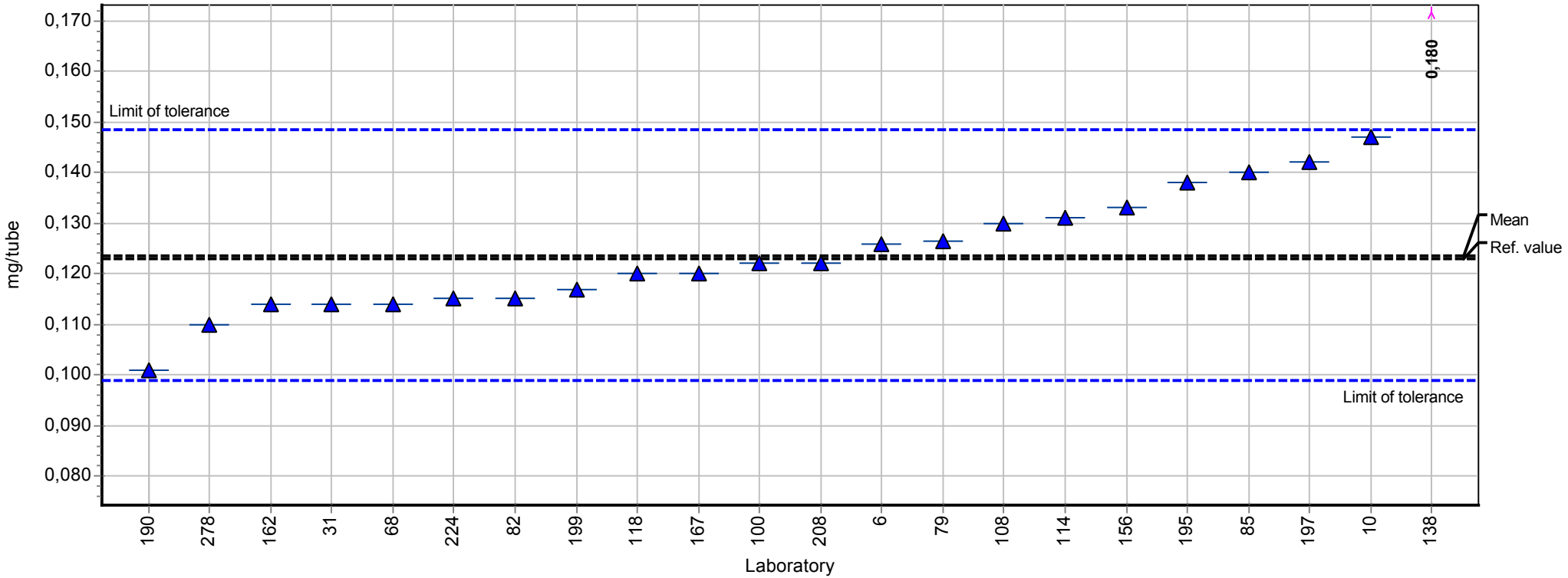
Summary results

Measurand:	**Toluene**	**Mean:**	**0,421 mg/tube**
Sample:	**1**	**Reproducibility s.d.:**	**0,031 mg/tube**
Method:	**ISO 5725-2**	**Relative reproducibility s.d.:**	**7,39%**
No. of laboratories:	**21**	**Reference value:**	**0,420 mg/tube**
Relative target s.d.:	**10,00% (Limited)**	**Range of tolerance:**	**0,337 - 0,505 mg/tube (|Z-Score| <= 2,00)**



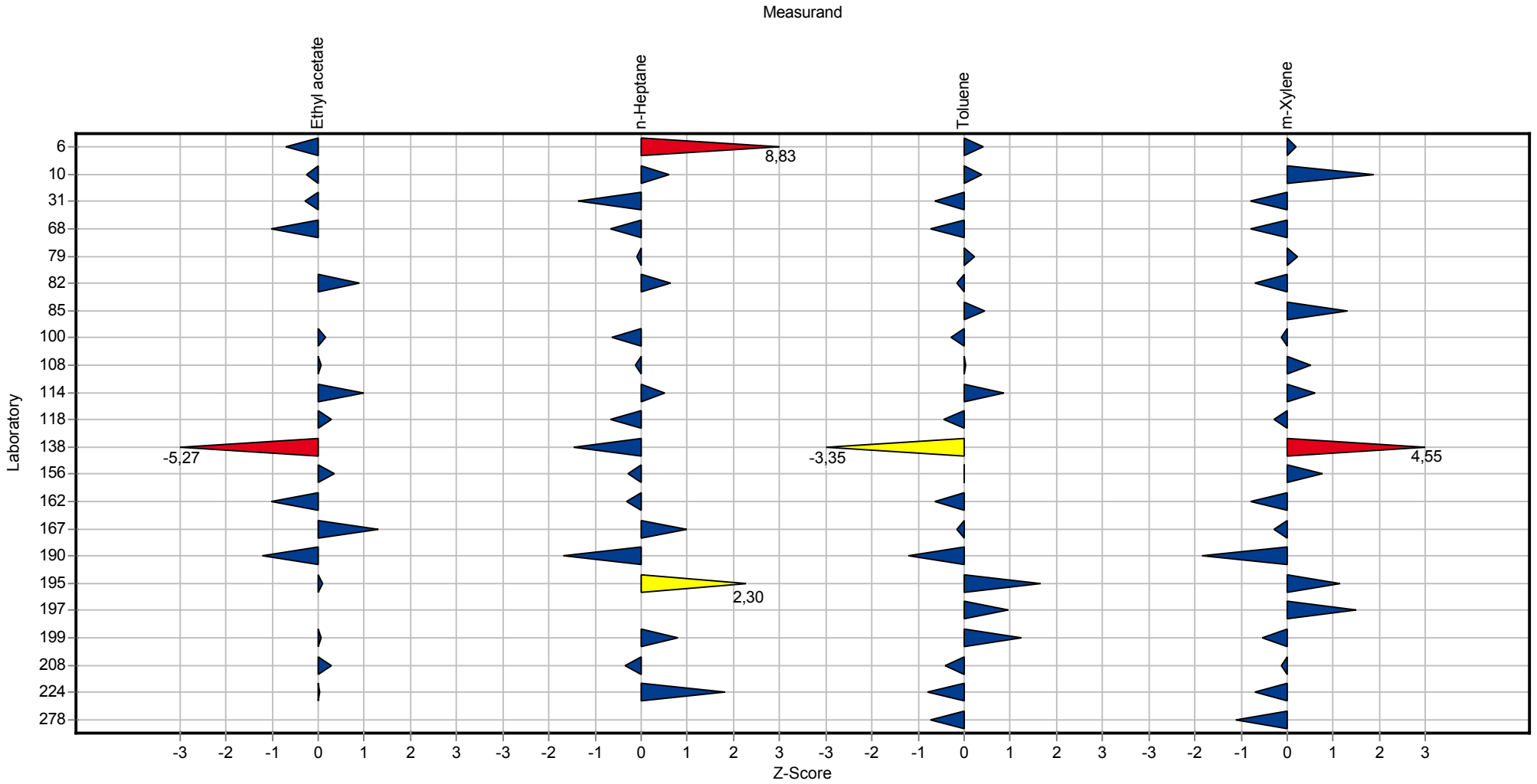
Summary results

Measurand:	**m-Xylene**	**Mean:**	**0,124 mg/tube**
Sample:	**1**	**Reproducibility s.d.:**	**0,012 mg/tube**
Method:	**ISO 5725-2**	**Relative reproducibility s.d.:**	**9,49%**
No. of laboratories:	**21**	**Reference value:**	**0,123 mg/tube**
Relative target s.d.:	**10,00% (Limited)**	**Range of tolerance:**	**0,099 - 0,148 mg/tube (|Z-Score| <= 2,00)**



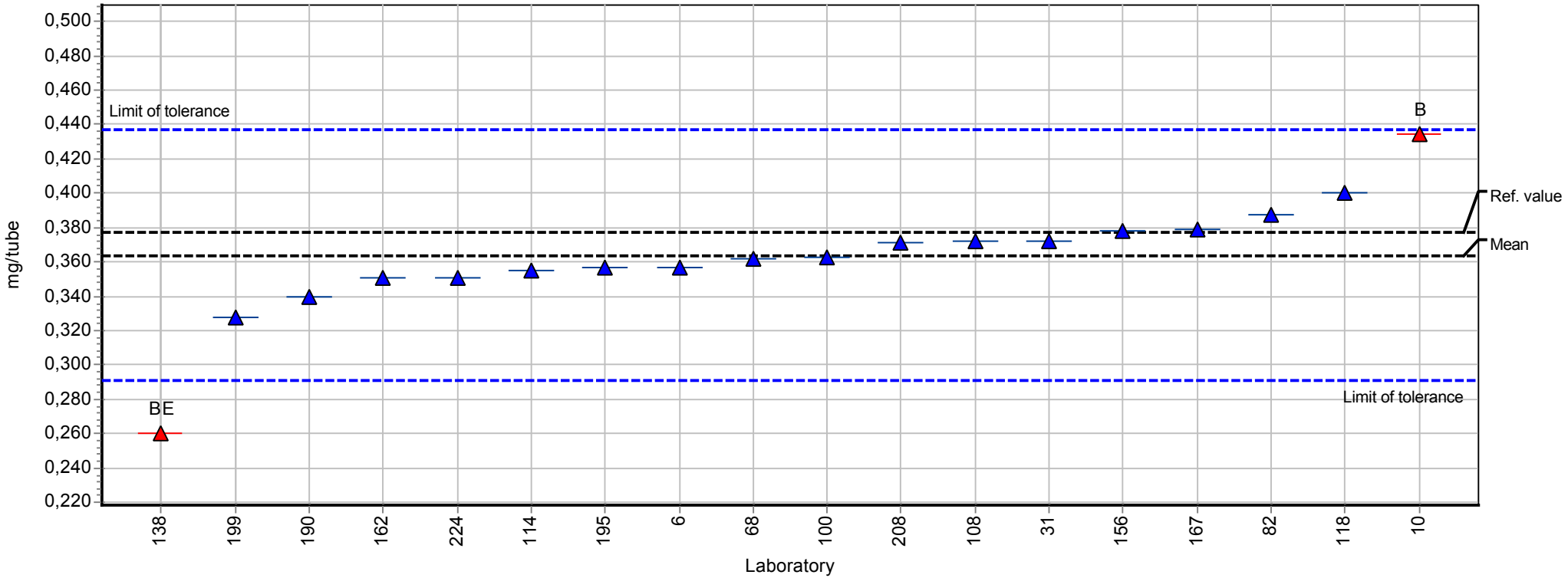
Sample chart of Z-Scores

Sample 1



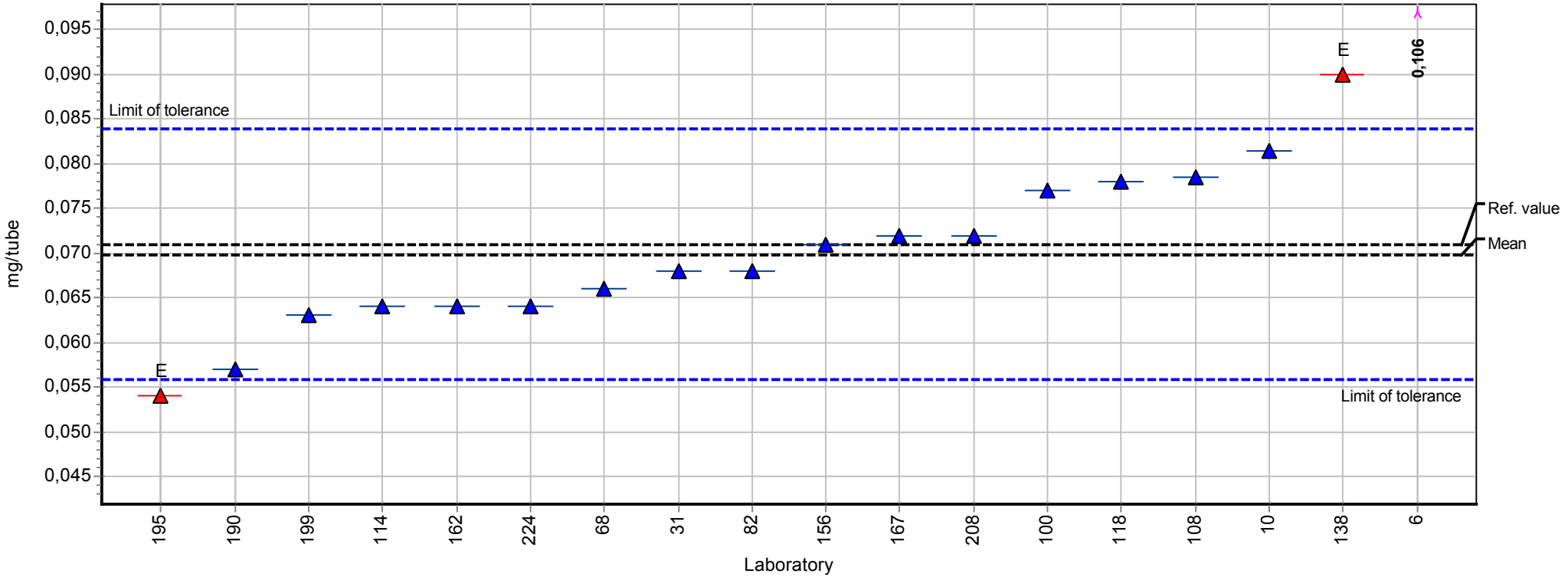
Summary results

Measurand:	**i-Butyl acetate**	**Mean:**	**0,364 mg/tube**
Sample:	**2**	**Reproducibility s.d.:**	**0,018 mg/tube**
Method:	**ISO 5725-2**	**Relative reproducibility s.d.:**	**4,92%**
No. of laboratories:	**16**	**Reference value:**	**0,377 mg/tube**
Relative target s.d.:	**10,00% (Limited)**	**Range of tolerance:**	**0,291 - 0,437 mg/tube (|Z-Score| <= 2,00)**



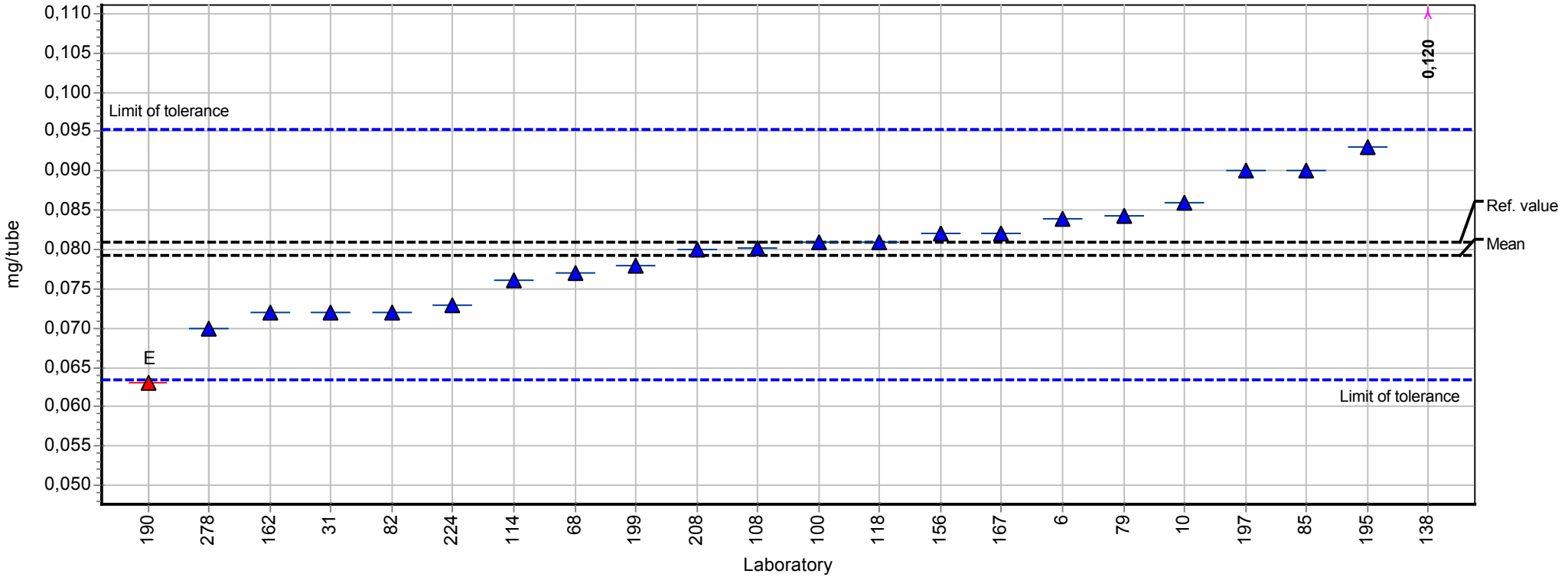
Summary results

Measurand:	**n-Butyl acetate**	**Mean:**	**0,070 mg/tube**
Sample:	**2**	**Reproducibility s.d.:**	**0,009 mg/tube**
Method:	**ISO 5725-2**	**Relative reproducibility s.d.:**	**13,05%**
No. of laboratories:	**17**	**Reference value:**	**0,071 mg/tube**
Relative target s.d.:	**10,00% (Limited)**	**Range of tolerance:**	**0,056 - 0,084 mg/tube (|Z-Score| <= 2,00)**



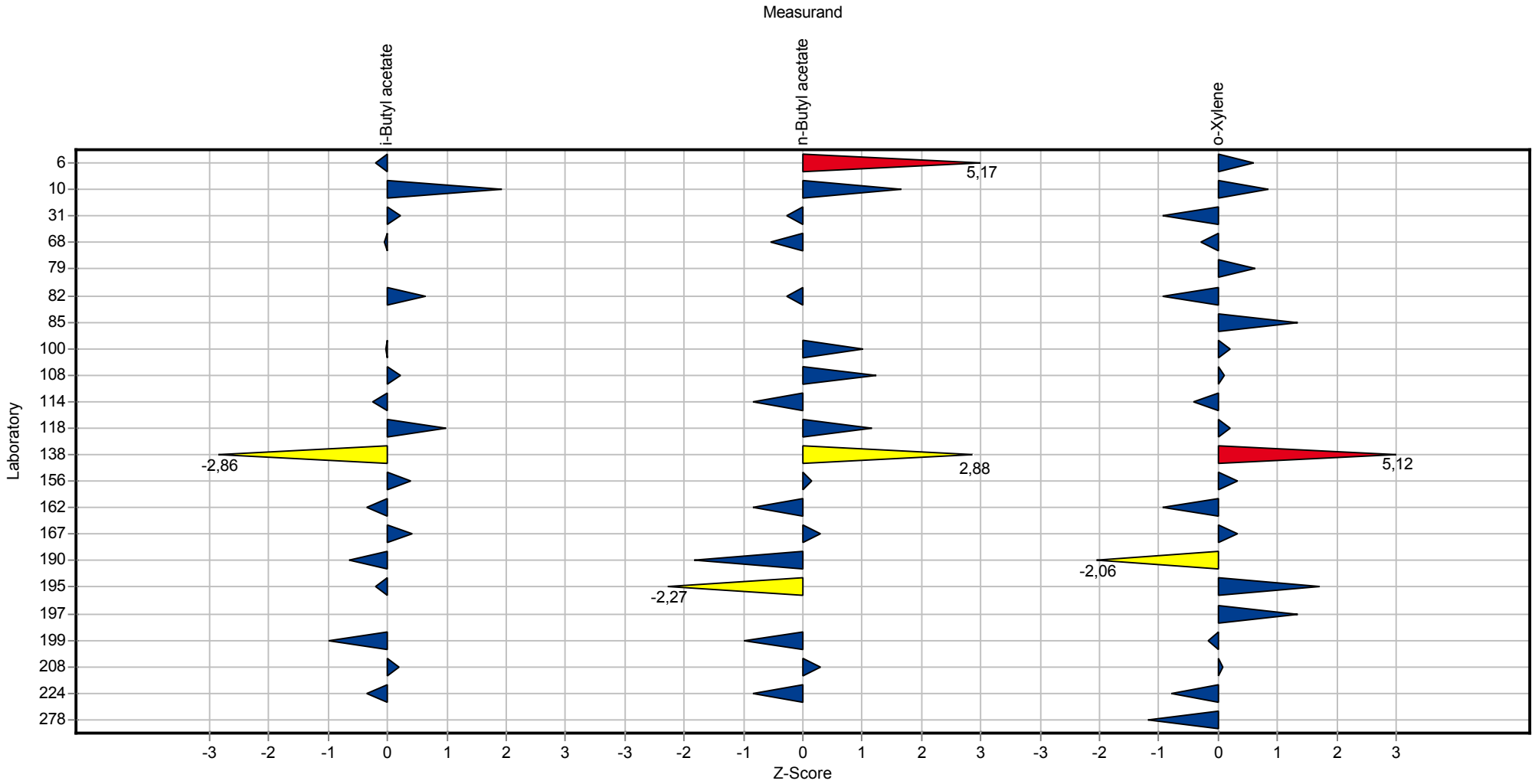
Summary results

Measurand:	**o-Xylene**	**Mean:**	**0,079 mg/tube**
Sample:	**2**	**Reproducibility s.d.:**	**0,007 mg/tube**
Method:	**ISO 5725-2**	**Relative reproducibility s.d.:**	**9,34%**
No. of laboratories:	**21**	**Reference value:**	**0,081 mg/tube**
Relative target s.d.:	**10,00% (Limited)**	**Range of tolerance:**	**0,063 - 0,095 mg/tube (|Z-Score| <= 2,00)**



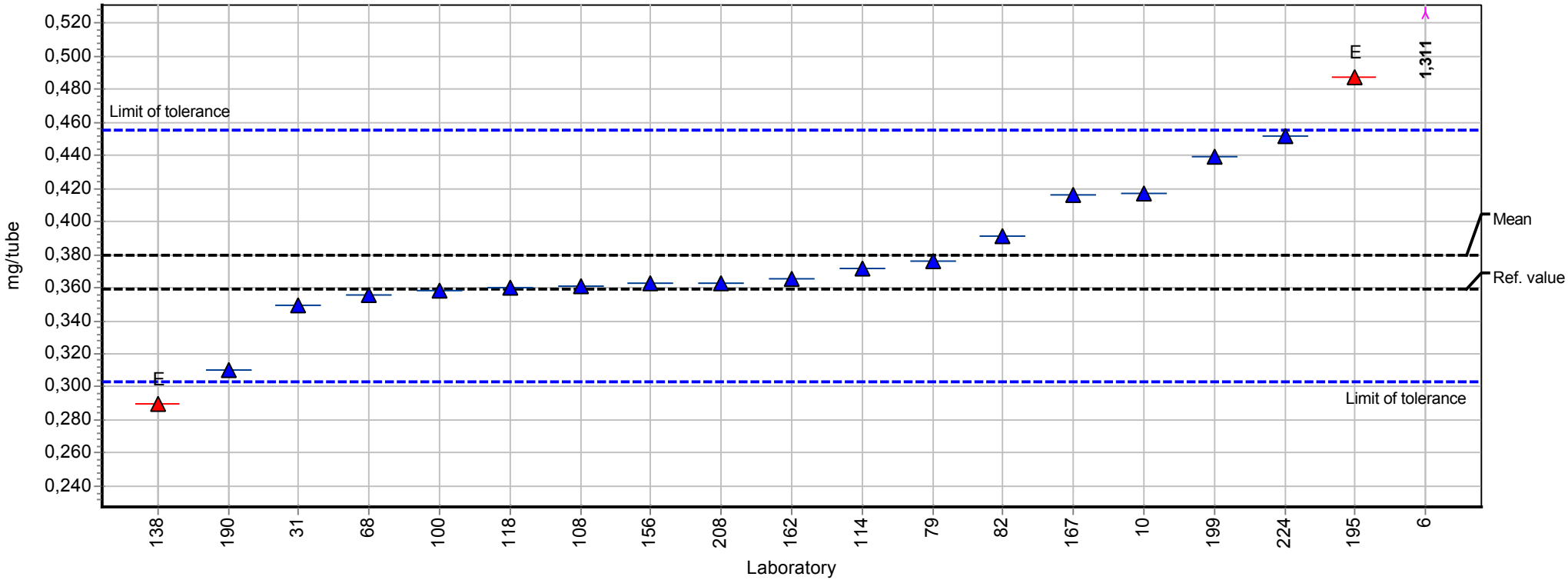
Sample chart of Z-Scores

Sample 2



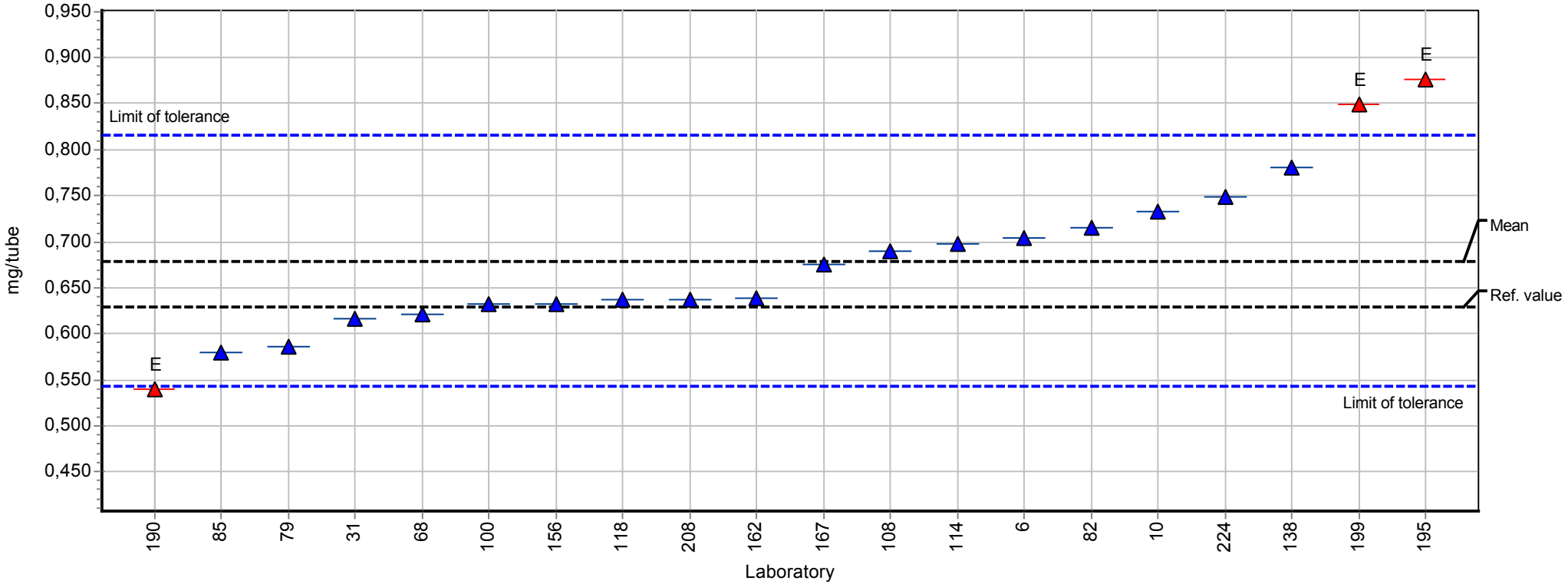
Summary results

Measurand:	**n-Heptane**	**Mean:**	**0,379 mg/tube**
Sample:	**3**	**Reproducibility s.d.:**	**0,048 mg/tube**
Method:	**ISO 5725-2**	**Relative reproducibility s.d.:**	**12,72%**
No. of laboratories:	**18**	**Reference value:**	**0,359 mg/tube**
Relative target s.d.:	**10,00% (Limited)**	**Range of tolerance:**	**0,303 - 0,455 mg/tube (|Z-Score| <= 2,00)**



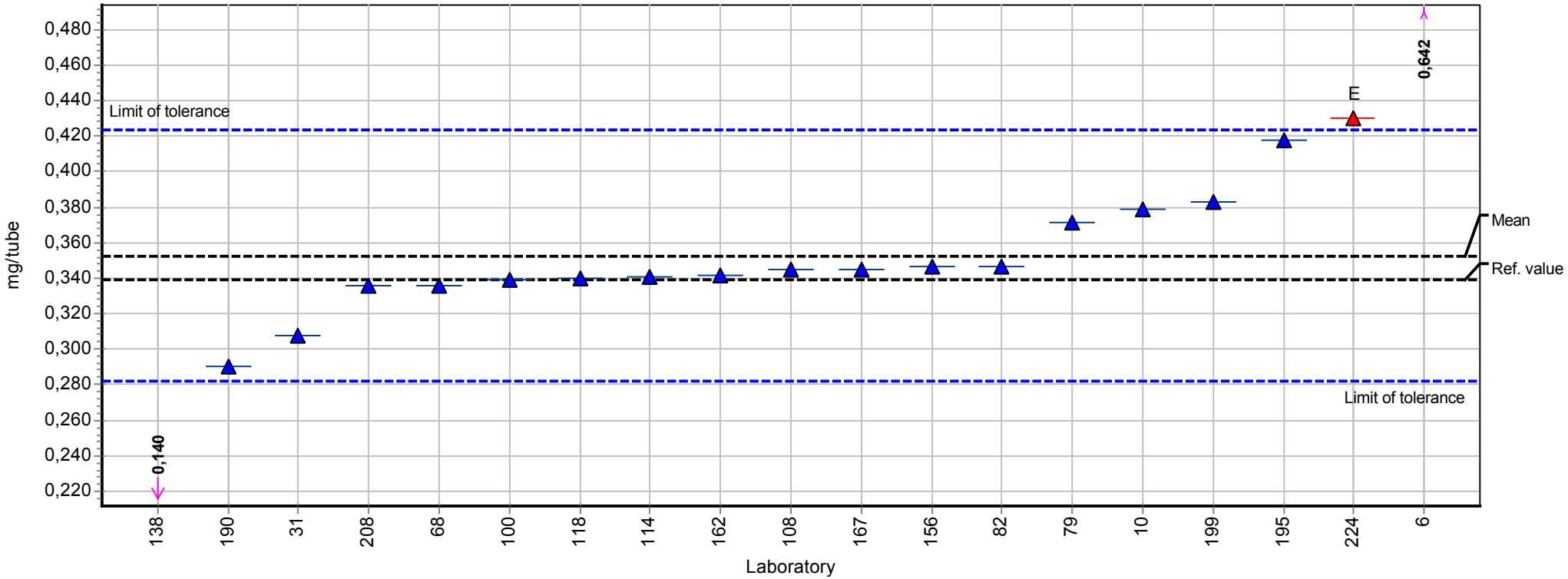
Summary results

Measurand:	**n-Hexane**	**Mean:**	**0,679 mg/tube**
Sample:	**3**	**Reproducibility s.d.:**	**0,087 mg/tube**
Method:	**ISO 5725-2**	**Relative reproducibility s.d.:**	**12,76%**
No. of laboratories:	**20**	**Reference value:**	**0,630 mg/tube**
Relative target s.d.:	**10,00% (Limited)**	**Range of tolerance:**	**0,544 - 0,815 mg/tube (|Z-Score| <= 2,00)**



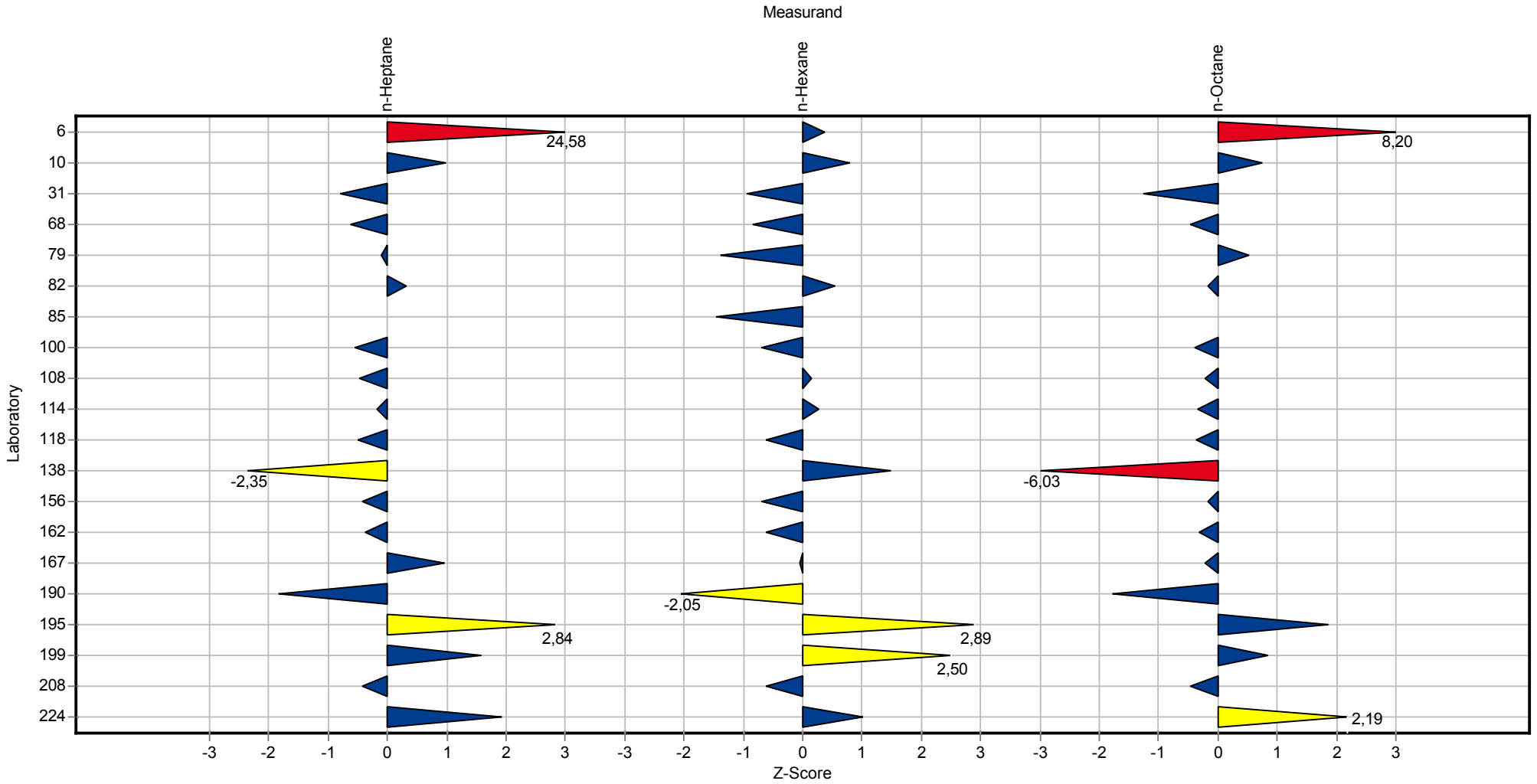
Summary results

Measurand:	**n-Octane**	**Mean:**	**0,353 mg/tube**
Sample:	**3**	**Reproducibility s.d.:**	**0,035 mg/tube**
Method:	**ISO 5725-2**	**Relative reproducibility s.d.:**	**9,89%**
No. of laboratories:	**17**	**Reference value:**	**0,339 mg/tube**
Relative target s.d.:	**10,00% (Limited)**	**Range of tolerance:**	**0,282 - 0,423 mg/tube (|Z-Score| <= 2,00)**



Sample chart of Z-Scores

Sample 3



Questions and Answers

Participant	Analytical method
6	7733 / 7732 / 7322
10	NFX43-267
31	IFA-Arbeitsmappe
68	Weder DFG noch IFA-Arbeitsmappe
79	BIA 6265
82	Hausmethode, angelehnt an DFG, Nr.: 3
85	interne Standard-Methode
100	X-43-267, Metropol/niosh
108	IFA 7732
114	According to the NF X 43-267; GC method: 40 to 300°C in 30min; injector temp: 220°C; MS method: 35 to 375
118	in Anlehnung an die VDI 2100 Blatt 2
138	BGIA- Verfahren
156	Laboreigene Methode
162	Hausmethode mit ISTD i-Oktan
167	Capillary Gas Chromatography
190	7732, 7733, 7322
195	Internal
197	DIN EN 14662-2
199	Extraktion mit Lösemittel inclusive internem Standard und Schwefelkohlenstoff, anschließend Messung am GC/MS
208	Own, based on NIOSH and OSHA methods
224	inhouse method
278	Hausmethode (AA4/1 C-063)

Participant	Desorption solution	Volume of desorption solution	Carrier gas	Injection
6	ternäres Gemisch	10 ml	Helium	split
10	CS2	1/1	helium	split
31	CH2Cl2:CS2:Methanol 60:35:5	2,5 mL	He	1 µL
68	CS2	1 ml	Helium	split
79	CS2	0,5 ml	Wasserstoff	split

Participant	Desorption solution	Volume of desorption solution	Carrier gas	Injection
82	CS2/Isopropanol 80/20	1 mL	Stickstoff	Split
85	CS2	1 mL	Stickstoff	splitless
100	CS2	2	helium	split
108	Schwefelkohlenstoff	10 ml	Helium	split
114	CS2	3mL	Helium	1µL
118	CS2	2mL	Stickstoff	on-column
138	ternäres Gemisch			
156	Schwefelkohlenstoff	2 ml	Helium	split
162	CS2	1ml	Wasserstoff	Split
167	Carbon disulphide	1,5 mL	Helium	1,0 µl splitless, 250 °C
190	Ternäres Gemisch (CH2Cl2 : CS2 : MeOH) = 60 : 35 : 5	5 mL	Helium	1 µL
195	carbon disulphide + n-propylbenecen as internal standard	1mL	He	Split
197	Kohlenstoffdisulfid	10 mL	Helium 4.6	split
199	Dichlormethan	3 Milliliter	Helium	splitless
208	2% DMF in carbon disulfide	1,5 ml	Helium	Split
224	carbon disulfide	2 ml	He	split
278	Benzylalkohol	4 ml	Helium	1 ml Gasphase

Participant	Analytical column	Detector
6	DB-5 / DB-624	FID
10	Supelcowax 10 - SPB5	FID
31	60m VF-5 MS und 60m HP-Innowax	FID
68	Vocol von Supelco	FID
79	CP Sil 5CB	FID
82	Agilent HP-5, 30 m x 0,32 mm; 0,25 µm	FID
85	DB-5 / DB-WAX	FID
100	DB624	MS
108	ZB-5, 60m, 0,25mm, 1µm	Massendetektor
114	DB 5MS 60m*0.25mm*1µm (5% phenyl . methylpolysiloxane)	MS
118	CP Sil 5 CB / CB-Wax 57 CB	FID
138		FID

Participant	Analytical column	Detector
156	HP 5 / CP-Wax	FID
162	J&W Scietific (Agilent) 50m X 0.2mm X 0,5µm PONA	FID
167	Zebron Guardian ZB-5MS, 30 m, 0,25 mm id, 0,25 µm film thickness	FID, 310 C
190	Rxi-5ms 30m x 0.25mm ID x 1.00µm df	FID/MS
195	Elite-5 60 m x 0.25 mm id x 1.5 um	FID
197	HP-VOC 60m, ID 0,2mm, Filmdicke 1,12 µm	MSD
199	DB-5.625MS	5975C GC-MS-Triple-Axis
208	Agilent HP-5, HP-InnoWax	FID
224	BPX5 60m x 0.25 mm x 1.0 µm	MS
278	DB 624- 30 m, 0,25 mm, 1,4 µm	MSD

Participant	Data evaluation	Recovery rate	Date of analysis
6	interner Standard	nein	11. KW 2015
10	external	no	04/03/2015
31	interne Standardmethode	nein	03.03.2015
68	interner Standard	Nein	4.3.2015
79	interner Standard		13. KW 2015
82	interner Standard	Nein	03.03.2015
85	interner Standard	ja	04.03.2015
100	internal standard	yes	12mars2015
108	interner Standard	ja	02.03.2015
114	TurboMass		19/03/2015
118	interner Standard		09.03.2015
138		67 - 84 %	24.03.2015
156	ESTD	81,9 - 104,1	08.03.2015
162	Interner Standard	ja	01.03.2015
167	Internal standard *chloro benzene(	Yes	10.03.15
190	über den internen Standard	nein	26.03.2015
195	Internal standard	yes	09/03/2015
197	Interner Standard	ja	16.03.2015
199	; Identifizierung: GC-MS + Standards der einzelnen Verbindungen	nein	20.03.2015

Participant	Data evaluation	Recovery rate	Date of analysis
208	External standard		27/02/2015
224	internal standard	no	17/3/2015
278	Chemstation, Peakfläche	102 bis 103 %	23.03.2015