

Round-robin tests for in-house and external measuring stations - results and evaluation

Round-robin test aldehydes with own sampling 19 - 20 September 2017

Summary of laboratory test results

Sample 1

	Formaldehyde Z score		Acetaldehyde Z score		Propionaldehyde Z score		Butyraldehyde Z score	
Unit	mg/m ³		mg/m ³		mg/m ³		mg/m ³	
24	0.1031	0.91	0.333	1.51	0.489	0.55	0.825	0.60
37	0.0830	-1.22	0.210	-2.74 E	0.380	-1.80	0.630	-1.91
95	0.1000	0.58	0.320	1.06	0.520	1.22	0.880	1.30
101	0.0960	0.16	0.308	0.65	0.447	-0.36	0.731	-0.61
116	0.0956	0.12	0.297	0.27	0.456	-0.16	0.789	0.13
121	0.0931	-0.15	0.293	0.13	0.445	-0.40	0.768	-0.14
135	0.0990	0.48	0.297	0.27	0.504	0.87	0.809	0.39
138	0.1700	7.99 BE	0.310	0.72	0.470	0.14	0.780	0.02
152	0.0900	-0.48	0.274	-0.53	0.449	-0.31	0.789	0.13
154	0.0950	0.05	0.289	-0.01	0.475	0.25	0.771	-0.10
158	0.1120	1.85	0.286	-0.11	0.471	0.16	0.862	1.07
209	0.0920	-0.26	0.271	-0.63	0.446	-0.38	0.788	0.12
244	0.0953	0.09	0.290	0.04	0.507	0.95	0.790	0.15
262	0.0950	0.05	0.240	-1.70	0.440	-0.51	0.720	-0.75
288	0.0738	-2.19 E	0.321	1.10	0.453	-0.23	0.746	-0.42
-	-	--	-	--	-	--	-	--
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	0.0945		0.289		0.463		0.779	
Reproducibility s.d.	0.0089		0.032		0.034		0.060	
Rel. reproducibility s.d.	9.40 %		10.96 %		7.40 %		7.66 %	
Reference value	0.0930		0.265		0.450		0.770	
Target s.d.	0.0094		0.029		0.046		0.078	
Rel. target s.d.	10.00 %		10.00 %		10.00 %		10.00 %	
Lower limit of tolerance	0.0756		0.231		0.371		0.623	
Upper limit of tolerance	0.1134		0.347		0.556		0.934	
No. of laboratories that submitted results	15		15		15		15	

	Formaldehyde Z score	Acetaldehyde Z score	Propionaldehyde Z score	Butyraldehyde Z score
Type B outliers	1			
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	14	15	15	15
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: $ Z\text{-Score} > 3.5$				
L: Differing laboratory mean (Grubbs II)	Grubbs für 2			

Summary of laboratory test results

Sample 2

	Formaldehyde Z score		Acetaldehyde Z score		Butyraldehyde Z score	
Unit	mg/m ³		mg/m ³		mg/m ³	
24	0.2482	1.03	1.162	1.58	0.555	1.40
37	0.1400	-3.78 FE	0.640	-3.62 FE	0.350	-2.81 E
95	0.2400	0.66	1.090	0.87	0.530	0.89
101	0.2200	-0.23	1.043	0.40	0.440	-0.96
116	0.2070	-0.80	0.930	-0.73	0.447	-0.81
121	0.2220	-0.14	0.983	-0.20	0.467	-0.40
135	0.2300	0.22	1.013	0.10	0.500	0.27
138	0.3100	3.77 FE	0.990	-0.13	0.490	0.07
152	0.2130	-0.54	0.926	-0.77	0.478	-0.18
154	0.2180	-0.31	0.980	-0.23	0.480	-0.14
158	0.2600	1.55	0.975	-0.28	0.528	0.85
209	0.2150	-0.45	0.929	-0.74	0.483	-0.07
244	0.2264	0.06	1.007	0.04	0.499	0.26
262	0.2150	-0.45	1.010	0.07	0.450	-0.75
288	0.2115	-0.60	1.360	3.56 FE	0.603	2.38 E
-	-	--	-	--	-	--
Method	ISO 5725-2		ISO 5725-2		ISO 5725-2	
Assessment	Z <=2.00		Z <=2.00		Z <=2.00	
Mean	0.2251		1.003		0.487	
Reproducibility s.d.	0.0157		0.067		0.058	
Rel. reproducibility s.d.	6.96 %		6.64 %		11.82 %	
Reference value	0.2340		1.000		0.454	
Target s.d.	0.0225		0.100		0.049	
Rel. target s.d.	10.00 %		10.00 %		10.00 %	
Lower limit of tolerance	0.1801		0.802		0.389	
Upper limit of tolerance	0.2701		1.204		0.584	
No. of laboratories that submitted results	15		15		15	

	Formaldehyde Z score	Acetaldehyde Z score	Butyraldehyde Z score
Type F outliers	2	2	
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	13	13	15
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: $ Z\text{-Score} > 3.5$			
L: Differing laboratory mean (Grubbs II)	Grubbs für 2		

Summary of laboratory test results

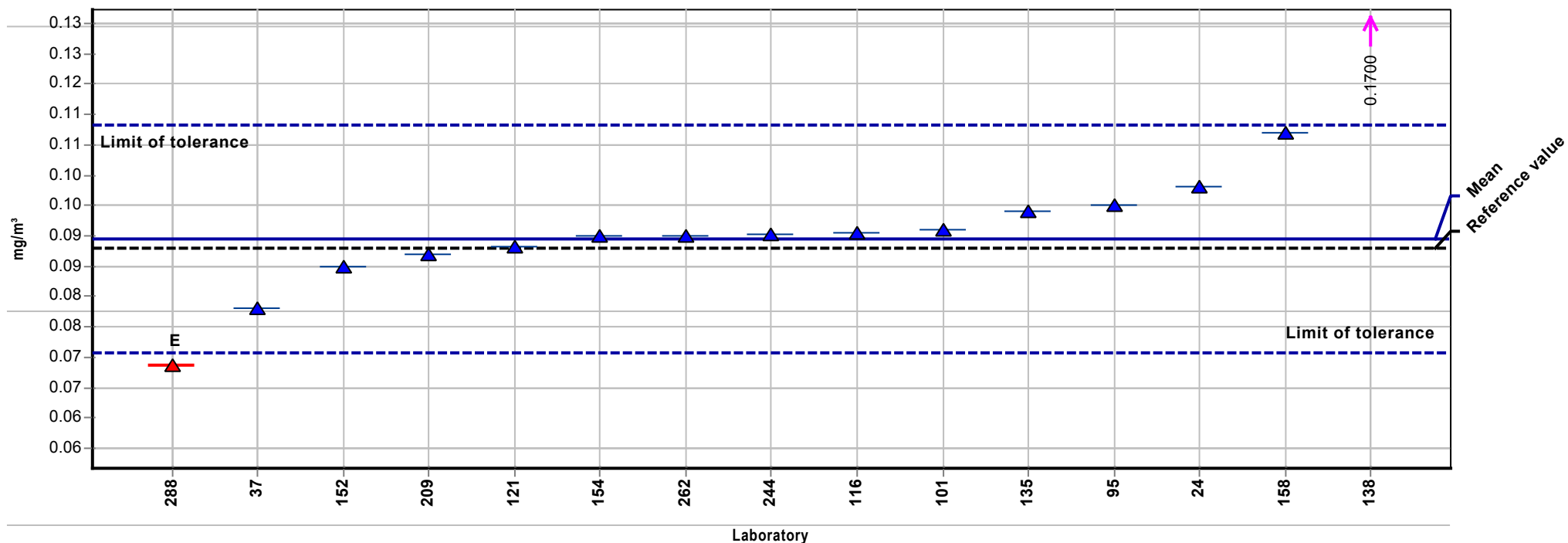
Sample 3

	Formaldehyde	Z score	Acetaldehyde	Z score	Butyraldehyde	Z score
Unit	mg/m ³		mg/m ³		mg/m ³	
24	0.1410	-0.52	0.580	1.29	0.923	-0.66
37	0.1100	-2.61 E	0.350	-3.19 E	0.730	-2.62 E
95	0.1600	0.76	0.590	1.49	1.130	1.43
101	0.1510	0.15	0.560	0.90	0.917	-0.73
116	0.1190	-2.00 E	0.424	-1.75	0.780	-2.11 E
121	0.1500	0.08	0.530	0.32	0.975	-0.14
135	0.1560	0.49	0.541	0.53	1.030	0.42
138	0.2000	3.45 E	0.570	1.10	1.030	0.42
152	0.1430	-0.39	0.499	-0.29	1.007	0.18
154	0.1520	0.22	0.546	0.63	0.997	0.08
158	0.1770	1.90	0.526	0.24	1.093	1.05
209	0.1460	-0.19	0.499	-0.29	1.024	0.36
244	0.1455	-0.22	0.526	0.25	1.004	0.15
262	0.1400	-0.59	0.450	-1.24	0.950	-0.39
288	0.1408	-0.54	0.720	4.02 FE	1.242	2.56 E
-	-	--	-	--	-	--
Method	ISO 5725-2		ISO 5725-2		ISO 5725-2	
Assessment	Z <=2.00		Z <=2.00		Z <=2.00	
Mean	0.1488		0.514		0.989	
Reproducibility s.d.	0.0211		0.066		0.126	
Rel. reproducibility s.d.	14.21 %		12.91 %		12.73 %	
Reference value	0.1550		0.519		1.030	
Target s.d.	0.0149		0.051		0.099	
Rel. target s.d.	10.00 %		10.00 %		10.00 %	
Lower limit of tolerance	0.1190		0.411		0.791	
Upper limit of tolerance	0.1785		0.616		1.187	
No. of laboratories that submitted results	15		15		15	

	Formaldehyde Z score	Acetaldehyde Z score	Butyraldehyde Z score
Type F outliers		1	
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	15	14	15
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: $ Z\text{-Score} > 3.5$			
L: Differing laboratory mean (Grubbs II)	Grubbs für 2		

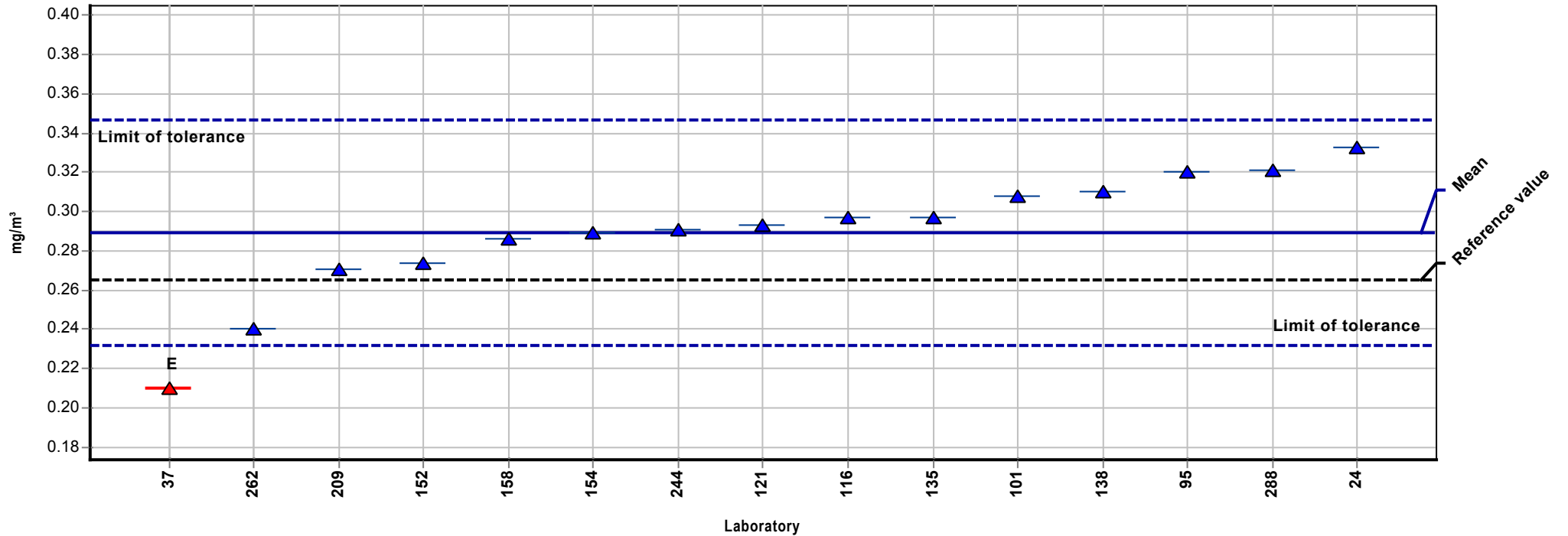
Summary results

Sample:	1	Mean:	0.0945 mg/m ³
Measurand:	Formaldehyde	Reproducibility s.d.:	0.0089 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	9.40%
Rel. target s.d.:	10.00%	Reference value:	0.0930 mg/m ³
No. of laboratories:	14	Range of tolerance:	0.0756 - 0.1134 mg/m ³ (Z-Score <= 2.00)



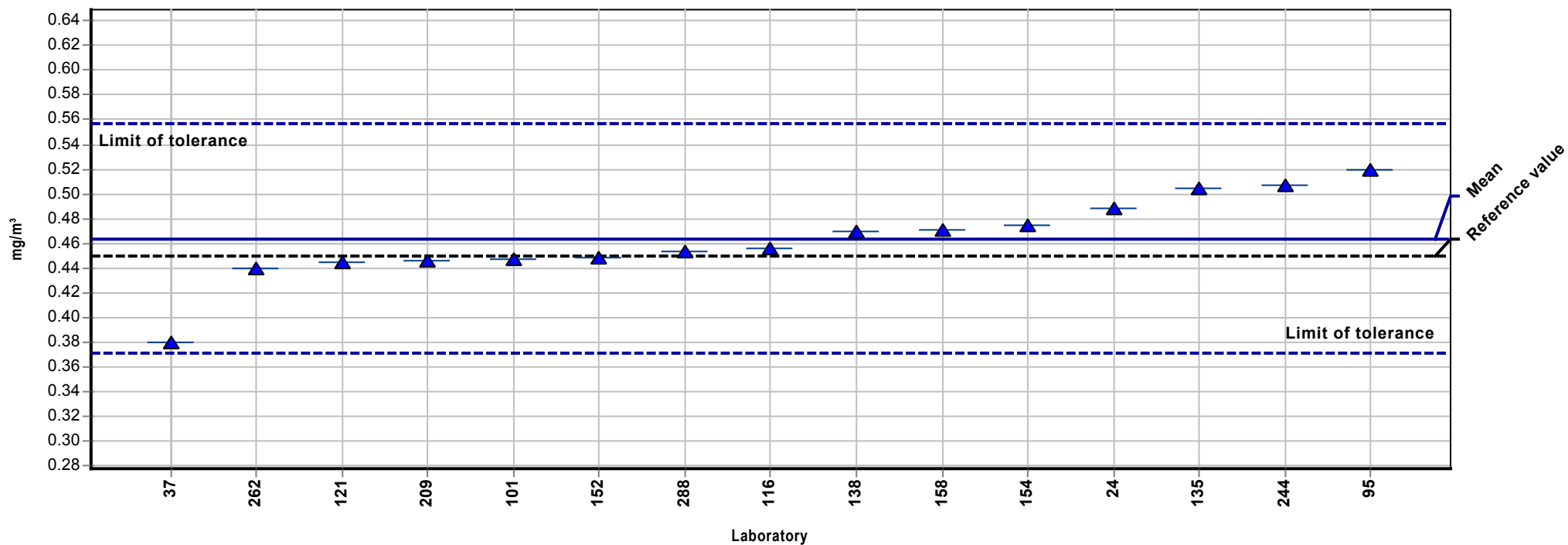
Summary results

Sample:	1	Mean:	0.289 mg/m ³
Measurand:	Acetaldehyde	Reproducibility s.d.:	0.032 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	10.96%
Rel. target s.d.:	10.00%	Reference value:	0.265 mg/m ³
No. of laboratories:	15	Range of tolerance:	0.231 - 0.347 mg/m ³ (Z-Score <= 2.00)



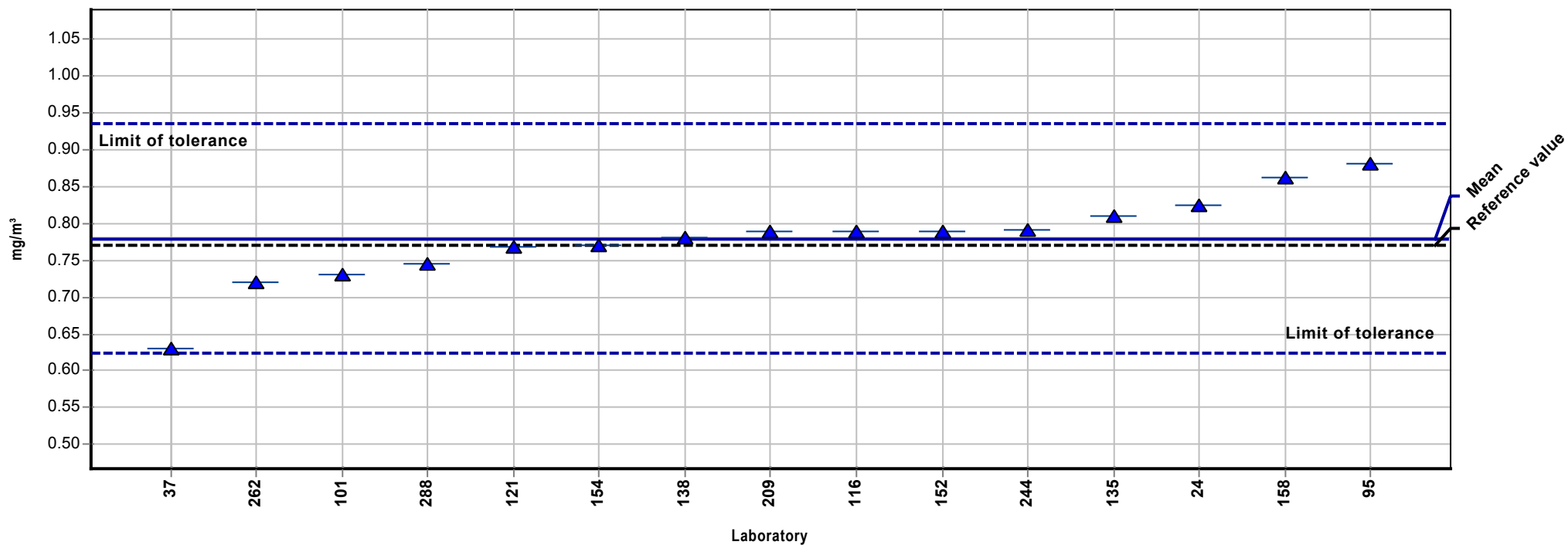
Summary results

Sample:	1	Mean:	0.463 mg/m ³
Measurand:	Propionaldehyde	Reproducibility s.d.:	0.034 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	7.40%
Rel. target s.d.:	10.00%	Reference value:	0.450 mg/m ³
No. of laboratories:	15	Range of tolerance:	0.371 - 0.556 mg/m ³ (Z-Score <= 2.00)



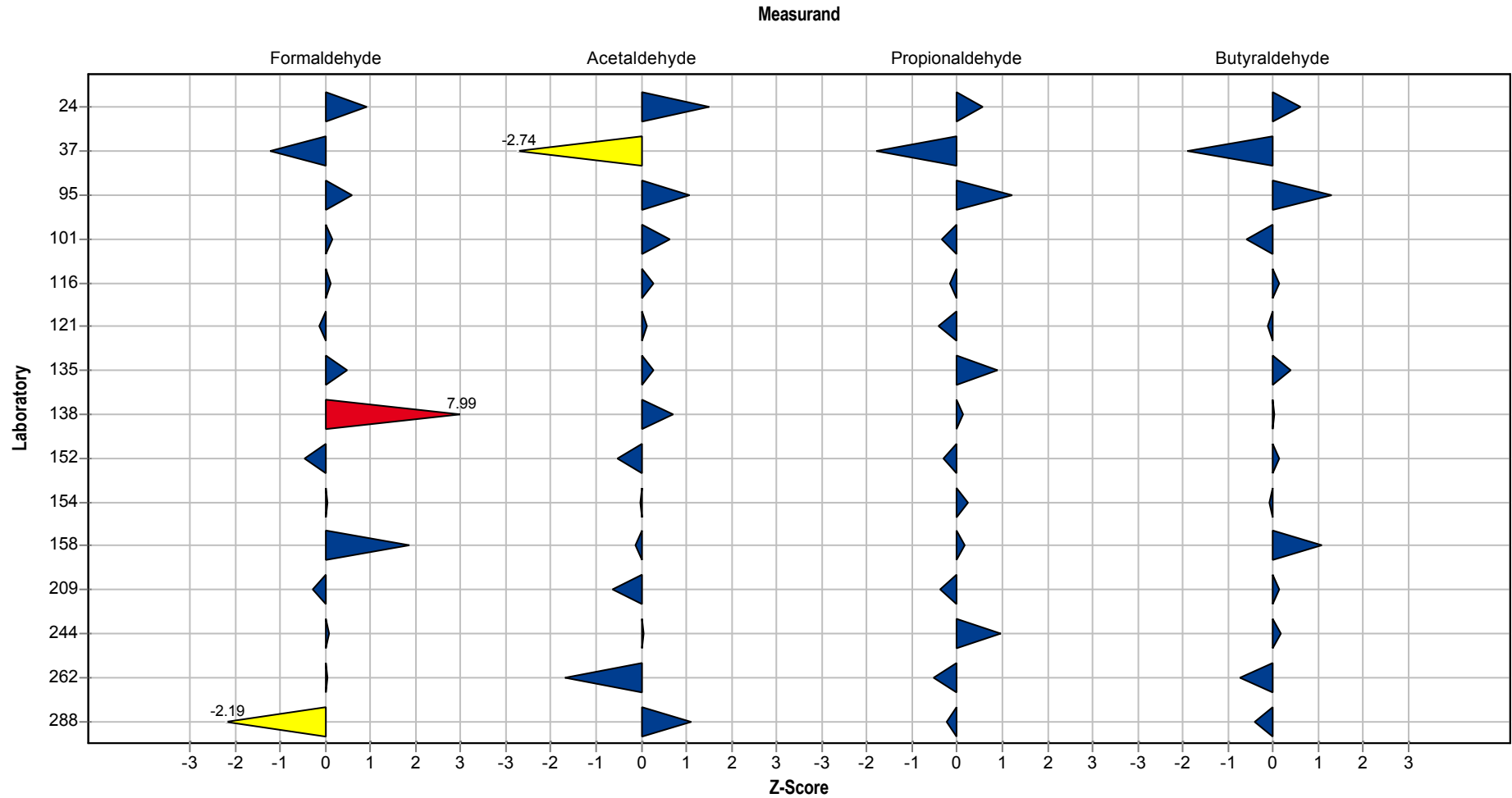
Summary results

Sample:	1	Mean:	0.779 mg/m ³
Measurand:	Butyraldehyde	Reproducibility s.d.:	0.060 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	7.66%
Rel. target s.d.:	10.00%	Reference value:	0.770 mg/m ³
No. of laboratories:	15	Range of tolerance:	0.623 - 0.934 mg/m ³ (Z-Score <= 2.00)



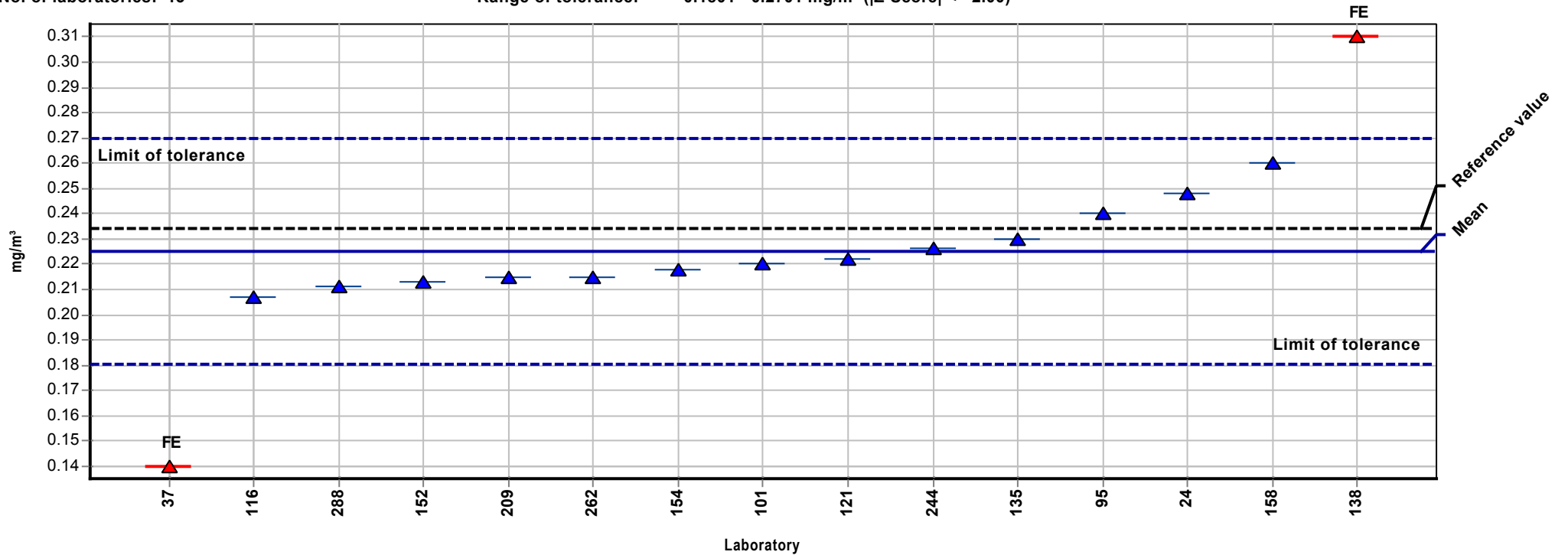
Sample chart of Z-Scores

Sample: 1



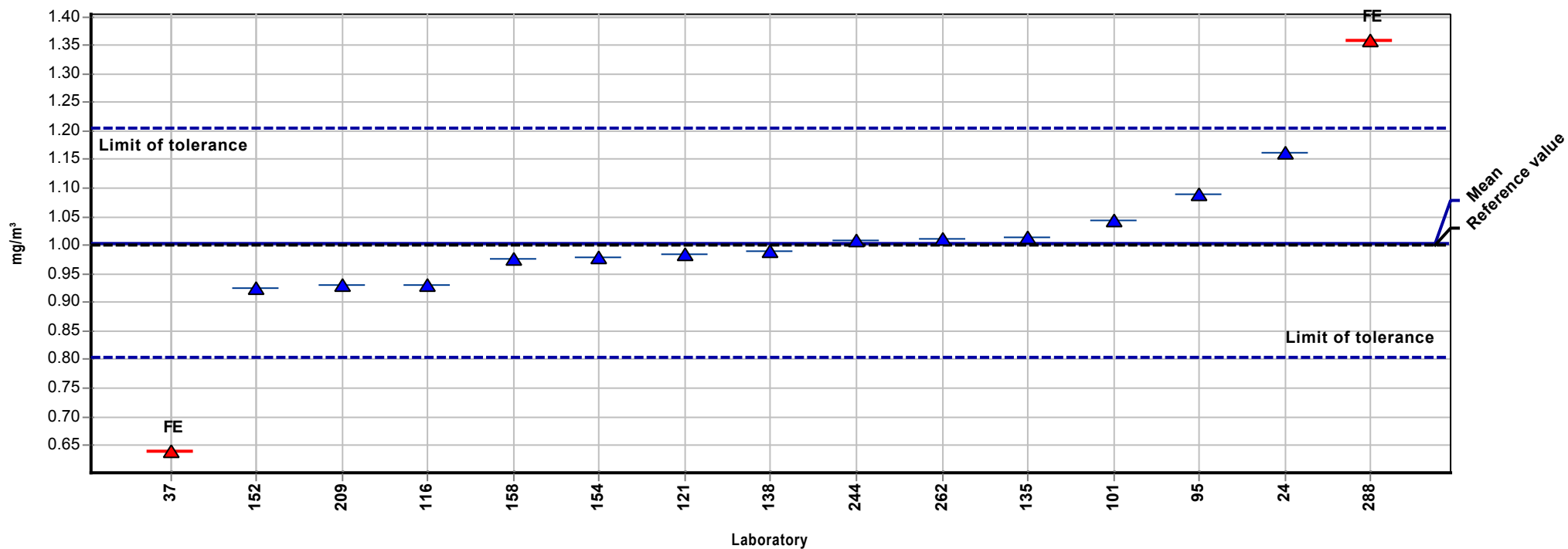
Summary results

Sample:	2	Mean:	0.2251 mg/m ³
Measurand:	Formaldehyde	Reproducibility s.d.:	0.0157 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	6.96%
Rel. target s.d.:	10.00%	Reference value:	0.2340 mg/m ³
No. of laboratories:	13	Range of tolerance:	0.1801 - 0.2701 mg/m ³ ($ Z\text{-Score} \leq 2.00$)



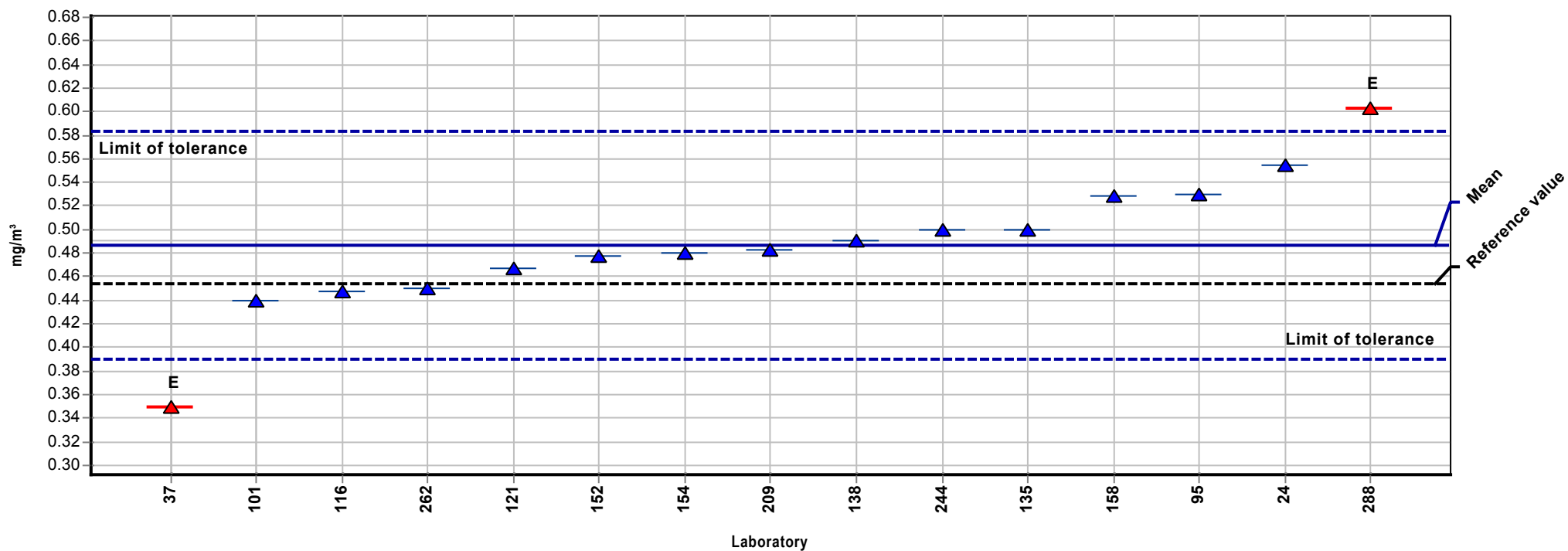
Summary results

Sample:	2	Mean:	1.003 mg/m ³
Measurand:	Acetaldehyde	Reproducibility s.d.:	0.067 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	6.64%
Rel. target s.d.:	10.00%	Reference value:	1.000 mg/m ³
No. of laboratories:	13	Range of tolerance:	0.802 - 1.204 mg/m ³ (Z-Score <= 2.00)



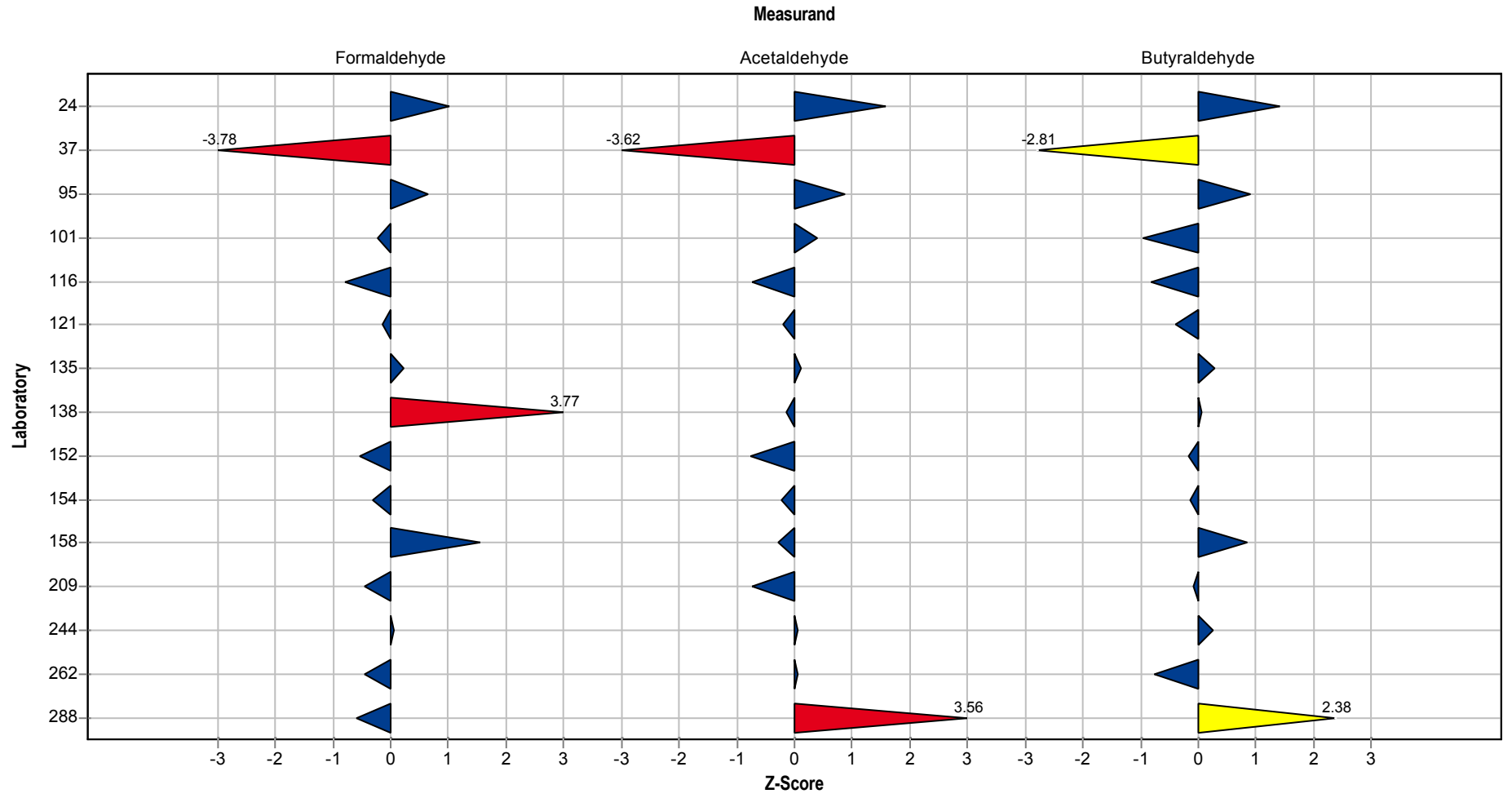
Summary results

Sample:	2	Mean:	0.487 mg/m ³
Measurand:	Butyraldehyde	Reproducibility s.d.:	0.058 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	11.82%
Rel. target s.d.:	10.00%	Reference value:	0.454 mg/m ³
No. of laboratories:	15	Range of tolerance:	0.389 - 0.584 mg/m ³ (Z-Score <= 2.00)



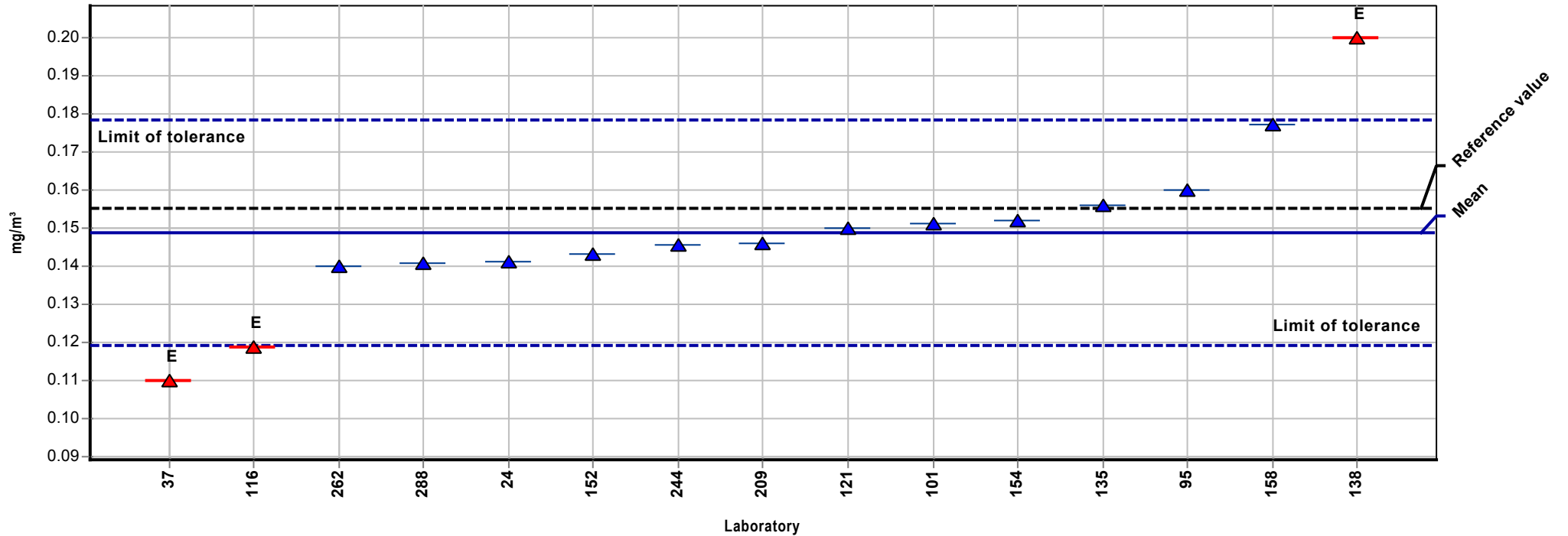
Sample chart of Z-Scores

Sample: 2



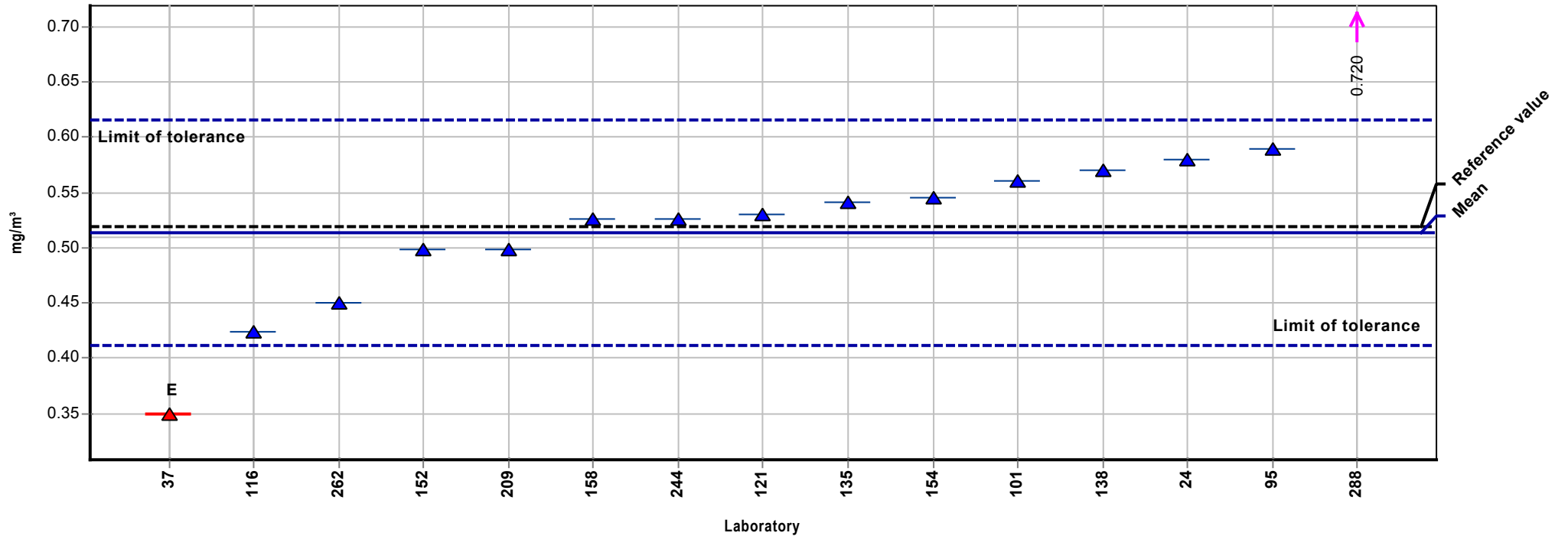
Summary results

Sample:	3	Mean:	0.1488 mg/m ³
Measurand:	Formaldehyde	Reproducibility s.d.:	0.0211 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	14.21%
Rel. target s.d.:	10.00%	Reference value:	0.1550 mg/m ³
No. of laboratories:	15	Range of tolerance:	0.1190 - 0.1785 mg/m ³ (Z-Score <= 2.00)



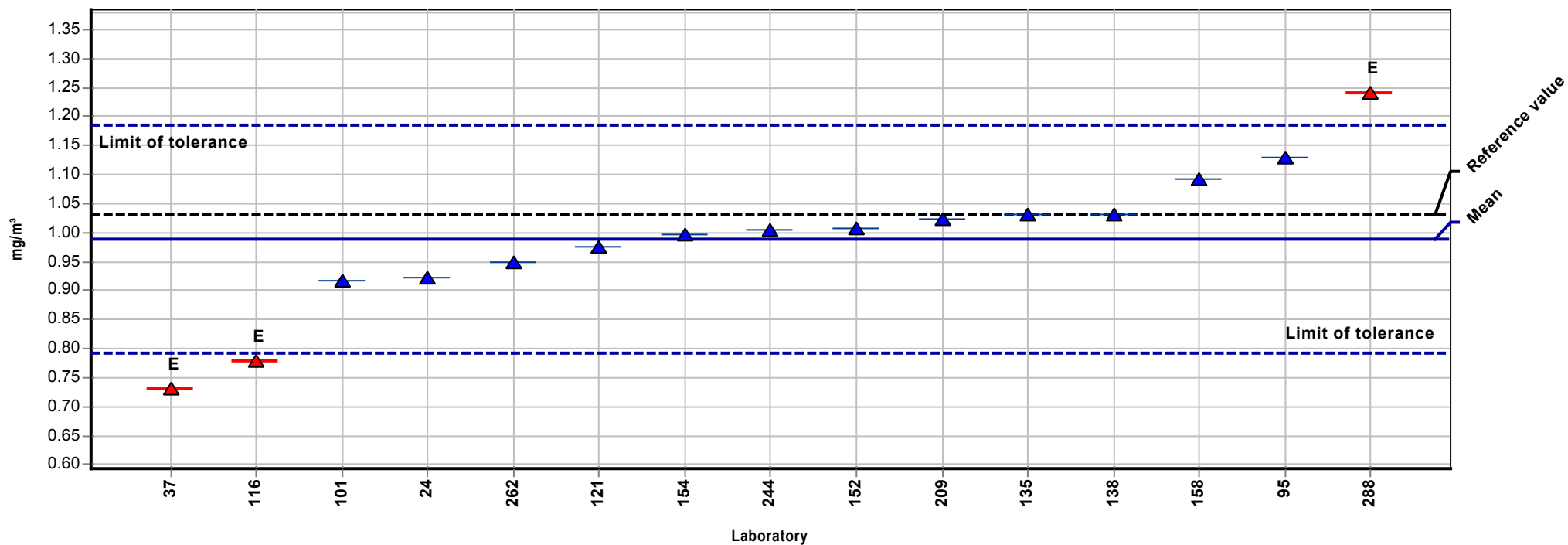
Summary results

Sample:	3	Mean:	0.514 mg/m ³
Measurand:	Acetaldehyde	Reproducibility s.d.:	0.066 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	12.91%
Rel. target s.d.:	10.00%	Reference value:	0.519 mg/m ³
No. of laboratories:	14	Range of tolerance:	0.411 - 0.616 mg/m ³ (Z-Score <= 2.00)



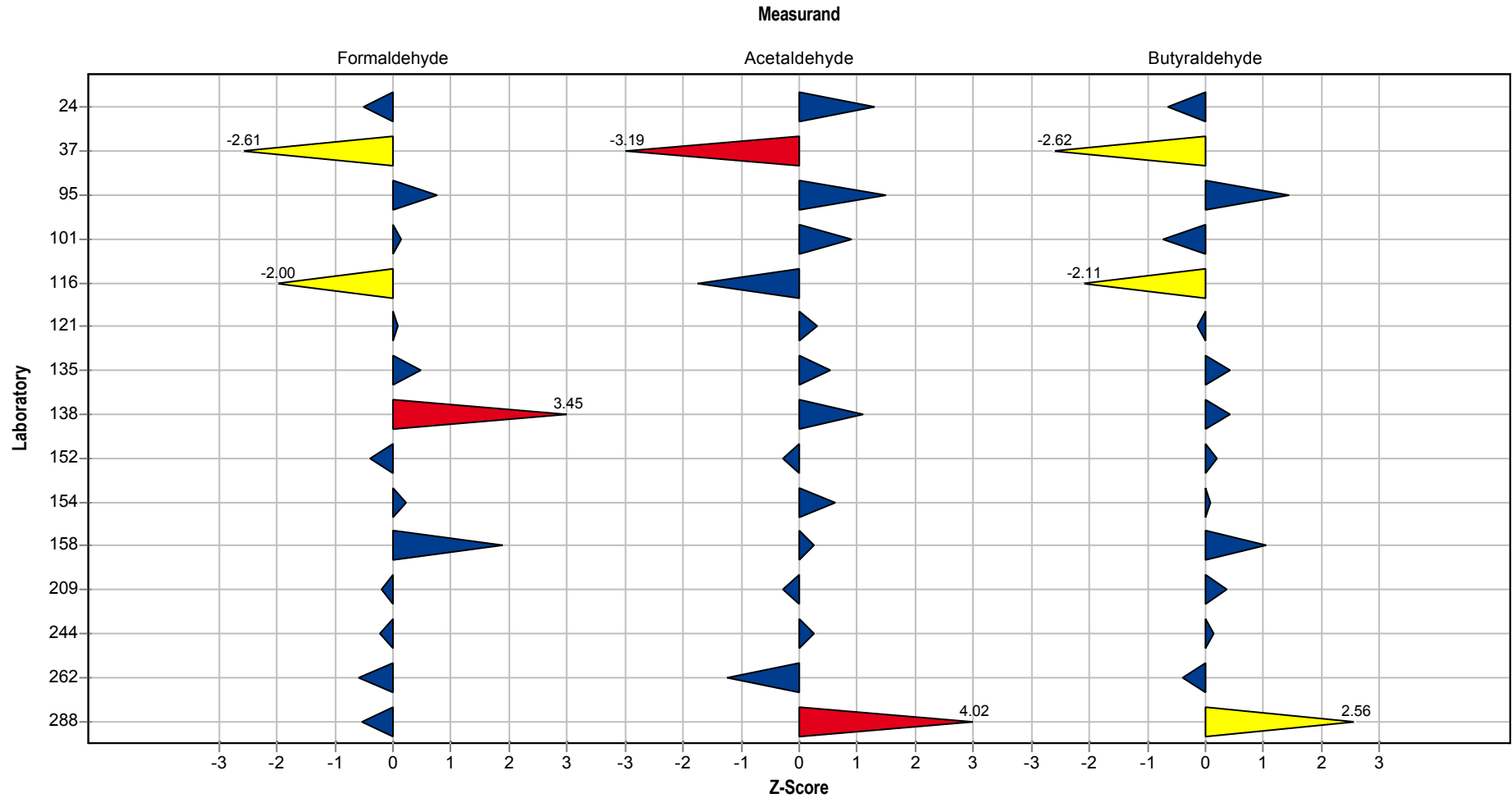
Summary results

Sample:	3	Mean:	0.989 mg/m ³
Measurand:	Butyraldehyde	Reproducibility s.d.:	0.126 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	12.73%
Rel. target s.d.:	10.00%	Reference value:	1.030 mg/m ³
No. of laboratories:	15	Range of tolerance:	0.791 - 1.187 mg/m ³ (Z-Score <= 2.00)



Sample chart of Z-Scores

Sample: 3



Questions and Answers

Participant	Sample carrier	Sampling pump	Sampling flow rate
24	DNPH/Silicagel	Desaga GS 301	1,0 L/min
37	Dual-Bed Lp DNPH Air Monitoring ORBO Sorbent Tubes, ORBO-555	Gilian PP1-Ex LFS-113 DC	0,30 - 0,33 l/min
95	LpDNPH S10 Cartridge 3mL, 350 mg SPE Tube von Supelco	GSA SG 4000	0,6 L/min
101	Lp DNPH S10 Cartridge (Supelco)	BIVOC, Gilian 3500	1,0L/min
116	Supelco DNPH	LfS 113	0,33-0,5 l/min
121	Supelco LpDNPH S10	GilAir Plus	0,15 L/min.
135	SUPELCO Lp DNPH S10	Holbach BiVOC2	1,0 l/min
138	SKC, 226-119	SKC, PCXR 8	0,5 l/min
152	DNPH (SKC)	Desaga GS301	1 L/min
154	Supelco LpDNPH S10	GilAir 5	0,333 L/min
158	Supelco LpDNPH S10	Gilian LFS-113DC	0,5 L/min
209	LpDNPH	GilAir, GSA2500	ca. 1.1 L/min
244	Supelco LpDNPH S10L Kartusche	SKC 210-1002 MTX	100 / 150 / 200 ml/min
262	SiOH-DNPH Glasröhrchen		

Participant	Flow rate measurement	Sampling time
24	entfällt	5-50 min
37	Analyt MTC Massenflussmesser GFM-17, MB 0 - 500 ml/min, kalibriert auf Luft	60 min
95	BIOS DryCal DC-2	30 min und 60 min
101	BIVOC, Gilian 3500	60min bzw. 30min
116		120 Minuten
121	DryCal DC Lite	60 und 120 Minuten
135	Interner Massenstromsensor + externe Kontrolle mit Sensidyne Gilibrator 2	20 - 60 min
138	Analyt, 35813MLW	60 bzw. 120 Minuten
152	interner Massflowcontroller	0.5 h
154	Seifenblasenzähler Gilibrator 2	120 Minuten
158	BIOS Defender 510	20 min und 40 min
209	TSI 4100	25 - 45 min
244	Bios DryCal Defender 510	60 / 120 min

Aldehydes with sampling 1/2017

Participant	Analytical method	Start sample preparation
24	DIN ISO 16000-3	22.09.2017
37	In Anlehnung an IFA 6045	26.09.2017
95	Bestimmung von DNPH-Derivaten von Aldehyden und Ketonen mittels LC-DAD	25.09.2017
101	VDI 3862 Bl. 3	20.10.2017
121	HPLC (LA-SOP-015; L-SOP-036)	22.09.2017
135	DIN ISO 16000-3	26.09.2017
138	BGIA 6045	ab dem 23.09.2017
152	DIN-ISO-16000-3	28.09.2017
154	IFA 6045	28.09.2017
158	Bestimmung als Derivate von 2,4- Dinitrophenylhydrazin (2,4-DNPH) mittels Hochleistungs-Flüssigkeits-Chromatografie (HPLC) und UV-Absorption	25.09.2017
209	DIN-16000-3-001 HPLC	keine Angaben vom Labor
244	6045	25. - 28.09.2017
262	ISO 16000-3, Compendium Method TO-11A:1999	27.09.2017

Participant	Storage time after desorption	Date of analysis	Desorption solution	Volume of desorption solution
24	33 Tage, Kühlschrank	24.10.2017	Acetonitril	5 mL
37	24 Stunden im Kühlschrank	27.09. - 29.09.2017	Acetonitril	10 ml
95	2 Tage im Kühlschrank	27.09.17	Acetonitril	5 mL
101	nein	20.10.2017	Acetonitril	5ml
121	72 h bei 5 °C	22.09.2017 und 25.09.2017	Acetonitril	5 mL
135	nein	26.09.2017	Acetonitril	2 ml
138	ja, Kühlschrank	bis zum 24.10.2017	Acetonitril	10 ml
152	1 Tag, Raumtemperatur	29.09.2017	Acetonitril	5ml
154	bis zum 30.09.2017 im Kühlschrank bei 4 °C	28.09. - 30.09.2017	Acetonitril	1 ml
158	Nein	26.09.2017	Acetonitril	2 x 2 ml und auf 5 aufgefüllt
209	keine Angaben vom Labor	keine Angaben vom Labor	keine Angaben vom Labor	keine Angaben vom Labor
244	6 bzw 5 Tage im Kühlschrank	25. und 26.09.2017	ACN	2 x 2mL und auf 5 mL aufgefüllt
262	1 d, Kühlschrank	28.09.2017	ACN	5 ml

Participant	Chromatography system (HPLC)	Autosampler
24	Hersteller: Perkin Elmer, Typ: Flexa	ungekühlt, Betrieb bei RT
37	Agilent 1100 Series; DAD	nein

Aldehydes with sampling 1/2017

Participant	Chromatography system (HPLC)	Autosampler
95	Acquity Ultra Performance (Waters) mit PDA Detektor	ja, 7°C
101	Pumpe: Agilent Technologies 1100 (G1312 A); Detektor: DAD Agilent Technologies 1100 (G1315 B); Autosampler: LTC Analytics LC-PAL	nein
121	Agilent 1290	20 °C
135	Agilent 1290 Series	10 °C
138	ThermoFisher, HPLC 3000	nein
152	Vanquish UPLC (VH-P10-A, VH-D10-A, VH-A10-A)	Nein
154	Pumpe: 1200 Bin Pump SL, Agilent Technologies; Detektor 1200 DAD SL Agilent Technologies; Autosampler 12000 HiP-ALS Agilent Technologies;	nein
158	Agilent HPLC mit DAD-UV Detektor	Nein
209	keine Angaben vom Labor	keine Angaben vom Labor
244	VWR 5160, VWR 5430 DAD, VWR 5260+Thermostat	Ja 30 °C
262	Hitachi HPLC + Autosampler, ABSciex MS/MS	nein

Participant	Analytical column	Flow rate HPLC	Mobile phase
24	Chromasil Eternity XP C-18 150 * 2,1 mm	0,4 mL/min	Acetonitril / Wasser / Tetrahydrofuran (60/30/10)
37	Perfect Chrom 250 x 4,0 mm; C 18, 5µm	1,5 ml/min	Wasser / Acetonitril, Gradient
95	Accucore C18 100x2, 1mm (Thermo Scientific)	0,6 mL/min	A:) Acetonitril/Wasser/THF, B:) Acetonitril/Wasser
101	Phenomenex, Aqua 3u C18 125A	0,2ml/min	Gradient aus Laufmittel A (12,5% ACN + 12,5% THF + 75% Wasser) und Laufmittel B (ACN)
121	Prontosil C18	1 mL/Min.	60/40 Acetonitril/Wasser
135	M&N EC 250/4.6 Nucleodur 100-5 C18ec	2,25 ml/min	Acetonitril - THF - Wasser
138	Nulceosil C 18, 250 mm	1,4 ml/Minute	Wasser / Acetonitril / Ameisensäure
152	Grom-Sil 120 ODS-5, 200 x 3 mm, 3 mikro m	0.5 ml/min	Acetonitril:Wasser Gradient
154	Nucleodur C18 Isis 3µm, Macherey & Nagel	0,5 ml/min	Acetonitril / Wasser
158	Hypersil ODS 4.0 x 250mm 5 Micron	1,000 ml/min	Von 60% Acetonitril bis 100% Acetonitril in 30 min
209	keine Angaben vom Labor	keine Angaben vom Labor	keine Angaben vom Labor
244	Merck Purospher STAR RP-18 ec (3µm) 250-3	0,35	ACN / Wasser
262	Nucleoshell RP 18plus, 2,7 µm	0,5 ml/min	Gradient aus Wasser/Methanol und ACN

Participant	Wavelength	Column temperature	Recovery rate
24	360 nm	40 °C	Formaldehyd: 101 %, Acetaldehyd: 97,5 %, Propionaldehyd: 99,3 %, Butyraldehyd: 102 %
37	365 nm / 254 nm / 380 nm	40 °C	nein
95	360 nm	40°C	nein
101	365nm	40°C	nein

Aldehydes with sampling 1/2017

Participant	Wavelength	Column temperature	Recovery rate
121	354 nm	30 °C	ja
135	365 nm	45 °C	nein
138	360 nm	40 °C	
152	360 nm	40° C	nein
154	365	30 °C	nein
158	360nm	30°C	Es wurde ein unabhängiger Kontrollstandard verwendet
209	keine Angaben vom Labor	keine Angaben vom Labor	keine Angaben vom Labor
244	355	35°C	nein
262		30 °C	nein