

Proficiency testing for in-house and external measuring stations - results and evaluation

Proficiency testing scheme Aldehydes 2024 with own sampling 2

13 - 14 November 2024

Summary of laboratory test results

Sample 1

Laboratory	Acetaldehyde	Z score	Butyraldehyde	Z score	Formaldehyde	Z score	Propionaldehyde	Z score
Unit	mg/m ³		mg/m ³		mg/m ³		mg/m ³	
66	0.816	-0.69	0.127	-1.08	0.568	-0.26	0.148	0.00
77					0.586	0.04		
122	0.822	-0.62	0.125	-1.22	0.566	-0.30	0.141	-0.47
159	0.916	0.45	0.154	0.81	0.598	0.25	0.133	-1.01
170	0.493	-4.38 BE	0.110	-2.28 E	0.532	-0.88	0.102	-3.11 E
231	0.857	-0.22	0.137	-0.38	0.564	-0.33	0.147	-0.07
250	0.962	0.97	0.180	2.61 E	0.696	1.93 B	0.177	1.97
259	0.798	-0.89	0.138	-0.33	0.574	-0.15	0.144	-0.27
267	0.880	0.04	0.131	-0.82	0.608	0.43	0.161	0.87
284	0.913	0.41	0.154	0.81	0.592	0.15	0.162	0.95
285	0.907	0.35	0.164	1.51	0.621	0.65	0.171	1.55
298	0.880	0.04	0.145	0.18	0.630	0.80	0.135	-0.88
517	0.892	0.17	0.145	0.18	0.561	-0.38	0.155	0.47
-	-	--	-	--	-	--	-	--
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	
No. of laboratories that submitted results	12		12		13		12	
Mean	0.877		0.142		0.583		0.148	
Reproducibility s.d.	0.050		0.019		0.028		0.020	
Rel. reproducibility s.d.	5.65 %		13.24 %		4.81 %		13.47 %	
Reference value	0.855		0.145		0.553		0.157	
Target s.d.	0.088		0.014		0.058		0.015	
Rel. target s.d.	10.00 %		10.00 %		10.00 %		10.00 %	
Lower limit of tolerance	0.701		0.114		0.467		0.118	
Upper limit of tolerance	1.052		0.171		0.700		0.178	
Type B outliers	1				1			
Type E outliers	1		2				1	

Laboratory	Acetaldehyde	Z score	Butyraldehyde	Z score	Formaldehyde	Z score	Propionaldehyde	Z score
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	11		12		12		12	
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-Score >3.50								

Summary of laboratory test results

Sample 2

Laboratory	Acetaldehyde	Z score	Butyraldehyde	Z score	Formaldehyde	Z score
Unit	mg/m ³		mg/m ³		mg/m ³	
66	0.911	-0.87	0.333	-1.65	0.170	0.97
77					0.149	-0.39
122	0.933	-0.65	0.347	-1.30	0.144	-0.71
159	1.087	0.90	0.408	0.23	0.149	-0.39
170	0.923	-0.75	0.375	-0.60	0.142	-0.84
231	0.966	-0.31	0.383	-0.40	0.139	-1.03
250	1.076	0.79	0.472	1.83	0.173	1.18
259	0.923	-0.74	0.374	-0.64	0.150	-0.31
267	1.000	0.03	0.360	-0.97	0.162	0.47
284	1.028	0.31	0.426	0.68	0.153	-0.13
285	1.050	0.53	0.455	1.40	0.165	0.65
298	1.050	0.53	0.370	-0.73	0.170	0.97
517	1.021	0.24	0.485	2.16 E	0.148	-0.45
-	-	--	-	--	-	--
Method	ISO 5725-2		ISO 5725-2		ISO 5725-2	
Assessment	Z <=2.00		Z <=2.00		Z <=2.00	
No. of laboratories that submitted results	12		12		13	
Mean	0.997		0.399		0.155	
Reproducibility s.d.	0.064		0.050		0.012	
Rel. reproducibility s.d.	6.40 %		12.55 %		7.51 %	
Reference value	0.982		0.397		0.145	
Target s.d.	0.100		0.040		0.015	
Rel. target s.d.	10.00 %		10.00 %		10.00 %	
Lower limit of tolerance	0.798		0.319		0.124	
Upper limit of tolerance	1.197		0.479		0.186	
Type E outliers			1			
No. of laboratories after elimination of	12		12		13	

Laboratory	Acetaldehyde	Z score	Butyraldehyde	Z score	Formaldehyde	Z score
Outliers type A-D and F (without laboratories that only gave states but no measured values)						
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-Score >3.50						

Summary of laboratory test results

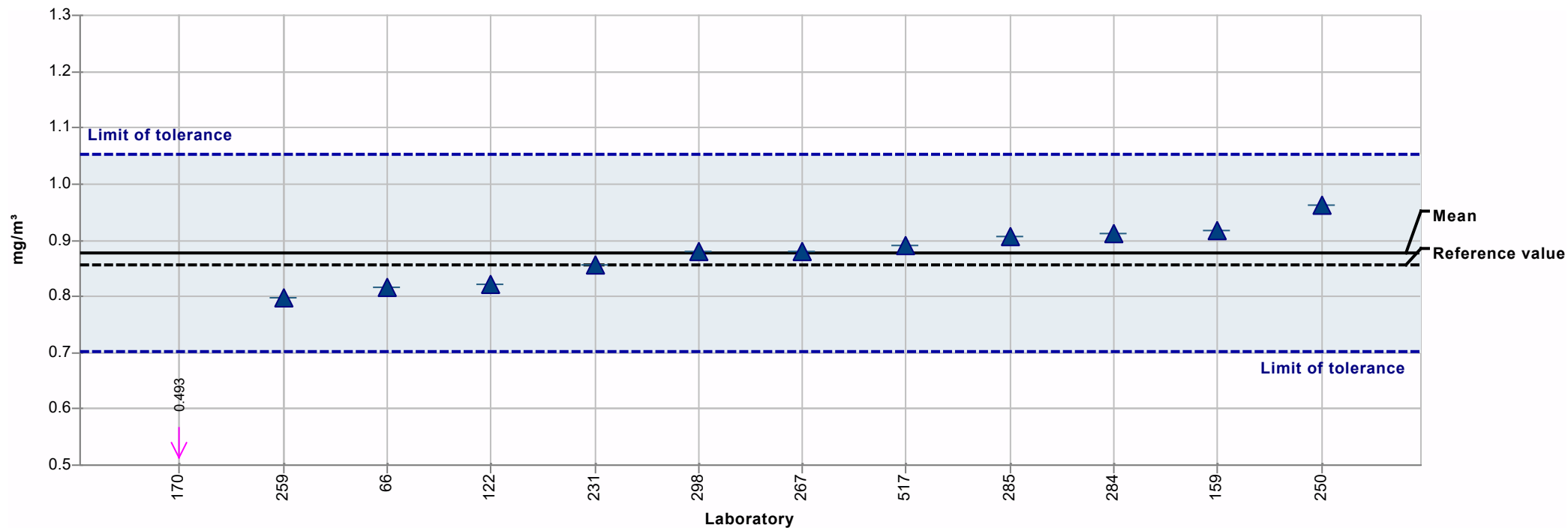
Sample 3

Laboratory	Acetaldehyde	Z score	Formaldehyde	Z score	Propionaldehyde	Z score
Unit	mg/m ³		mg/m ³		mg/m ³	
66	0.355	-0.51	0.408	-0.15	0.94	-1.27
77			0.428	0.35		
122	0.349	-0.67	0.397	-0.41	1.04	-0.37
159	0.376	0.05	0.399	-0.37	1.00	-0.76
170	0.220	-4.12 BE	0.390	-0.58	0.83	-2.33 E
231	0.364	-0.27	0.395	-0.46	1.12	0.34
250	0.398	0.64	0.460	1.11	1.22	1.28
259	0.339	-0.95	0.400	-0.35	1.05	-0.33
267	0.381	0.18	0.426	0.28	1.17	0.78
284	0.395	0.56	0.417	0.07	1.20	1.06
285	0.387	0.34	0.432	0.43	1.24	1.45
298	0.390	0.42	0.450	0.87	1.06	-0.21
517	0.382	0.21	0.382	-0.78	1.12	0.34
-	-	--	-	--	-	--
Method	ISO 5725-2		ISO 5725-2		ISO 5725-2	
Assessment	Z <=2.00		Z <=2.00		Z <=2.00	
No. of laboratories that submitted results	12		13		12	
Mean	0.374		0.414		1.08	
Reproducibility s.d.	0.020		0.024		0.12	
Rel. reproducibility s.d.	5.27 %		5.75 %		11.13 %	
Reference value	0.364		0.384		1.13	
Target s.d.	0.037		0.041		0.11	
Rel. target s.d.	10.00 %		10.00 %		10.00 %	
Lower limit of tolerance	0.299		0.331		0.87	
Upper limit of tolerance	0.449		0.497		1.30	
Type B outliers	1					
Type E outliers	1				1	

Laboratory	Acetaldehyde Z score	Formaldehyde Z score	Propionaldehyde Z score
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	11	13	12
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-Score >3.50			

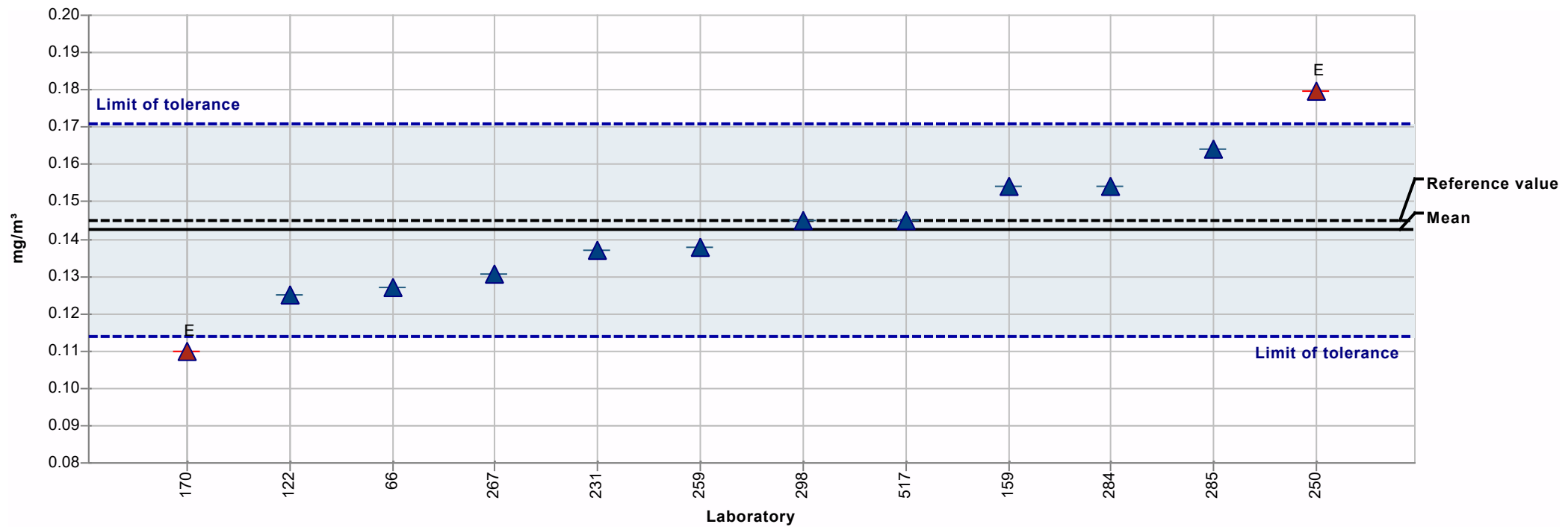
Summary results

Sample:	1	Mean:	0.877 mg/m³
Measurand:	Acetaldehyde	Reproducibility s.d.:	0.050 mg/m³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	5.65%
Rel. target s.d.:	10.00%	Reference value:	0.855 mg/m³
Number of laboratories in calculation: 11		Range of tolerance:	0.701 - 1.052 mg/m³ (Z-Score <= 2.00)



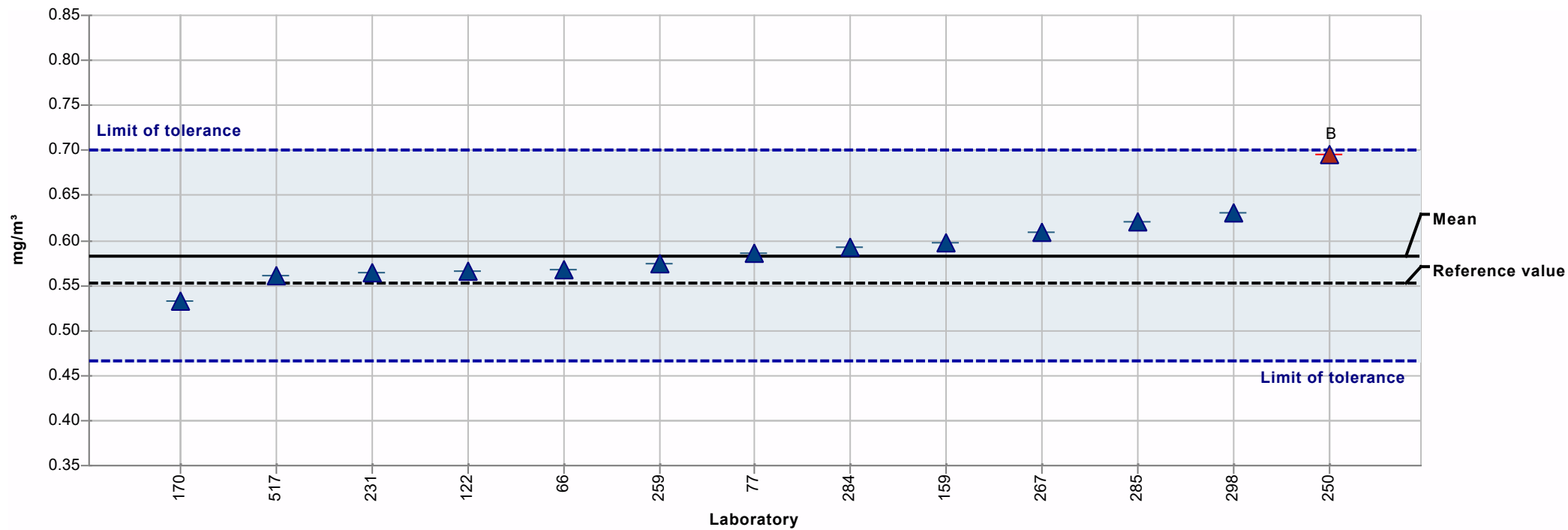
Summary results

Sample:	1	Mean:	0.142 mg/m³
Measurand:	Butyraldehyde	Reproducibility s.d.:	0.019 mg/m³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	13.24%
Rel. target s.d.:	10.00%	Reference value:	0.145 mg/m³
Number of laboratories in calculation: 12		Range of tolerance:	0.114 - 0.171 mg/m³ (Z-Score <= 2.00)



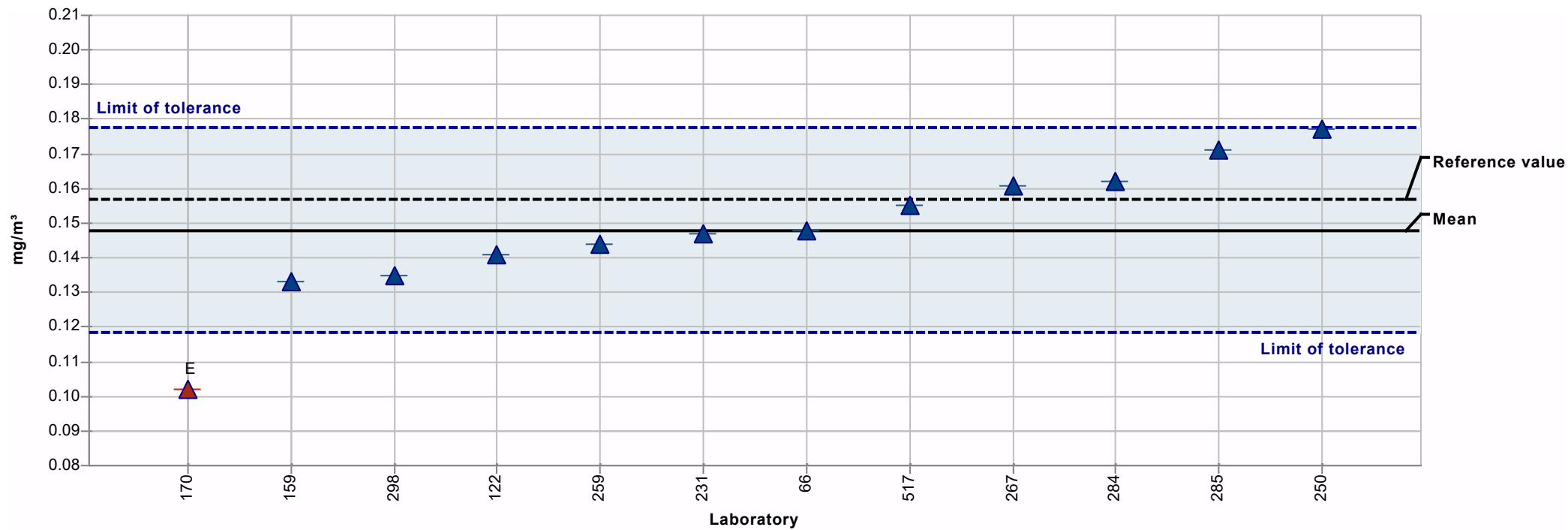
Summary results

Sample:	1	Mean:	0.583 mg/m³
Measurand:	Formaldehyde	Reproducibility s.d.:	0.028 mg/m³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	4.81%
Rel. target s.d.:	10.00%	Reference value:	0.553 mg/m³
Number of laboratories in calculation: 12		Range of tolerance:	0.467 - 0.700 mg/m³ (Z-Score <= 2.00)



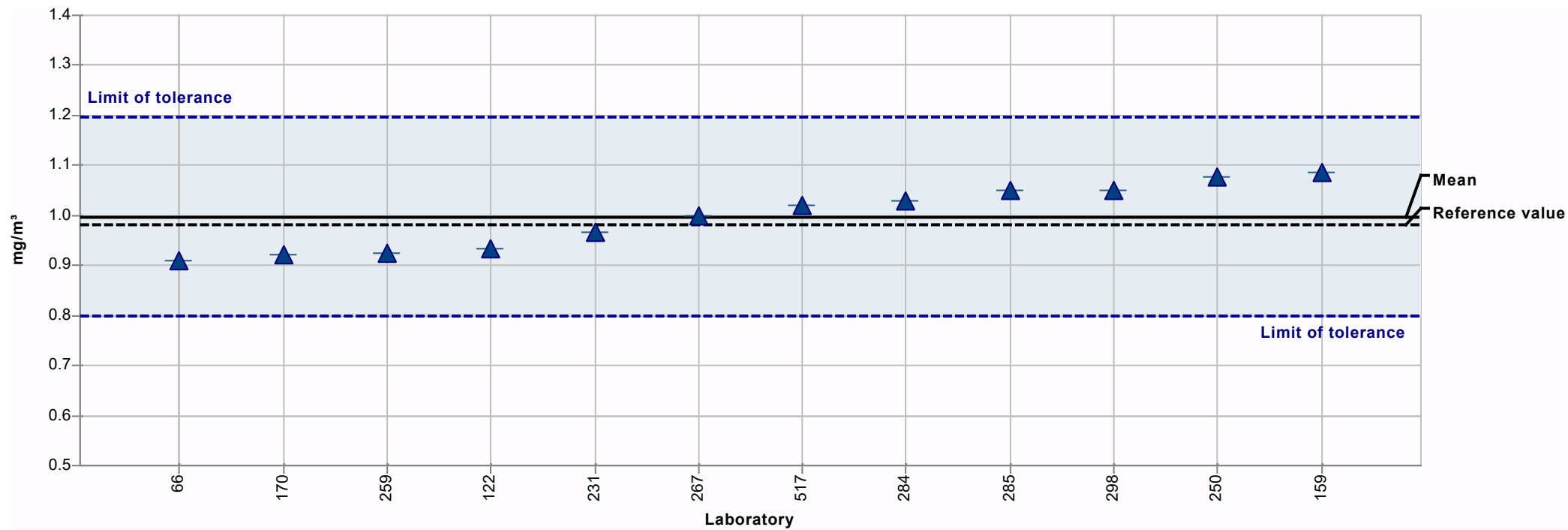
Summary results

Sample:	1	Mean:	0.148 mg/m³
Measurand:	Propionaldehyde	Reproducibility s.d.:	0.020 mg/m³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	13.47%
Rel. target s.d.:	10.00%	Reference value:	0.157 mg/m³
Number of laboratories in calculation: 12		Range of tolerance:	0.118 - 0.178 mg/m³ (Z-Score <= 2.00)



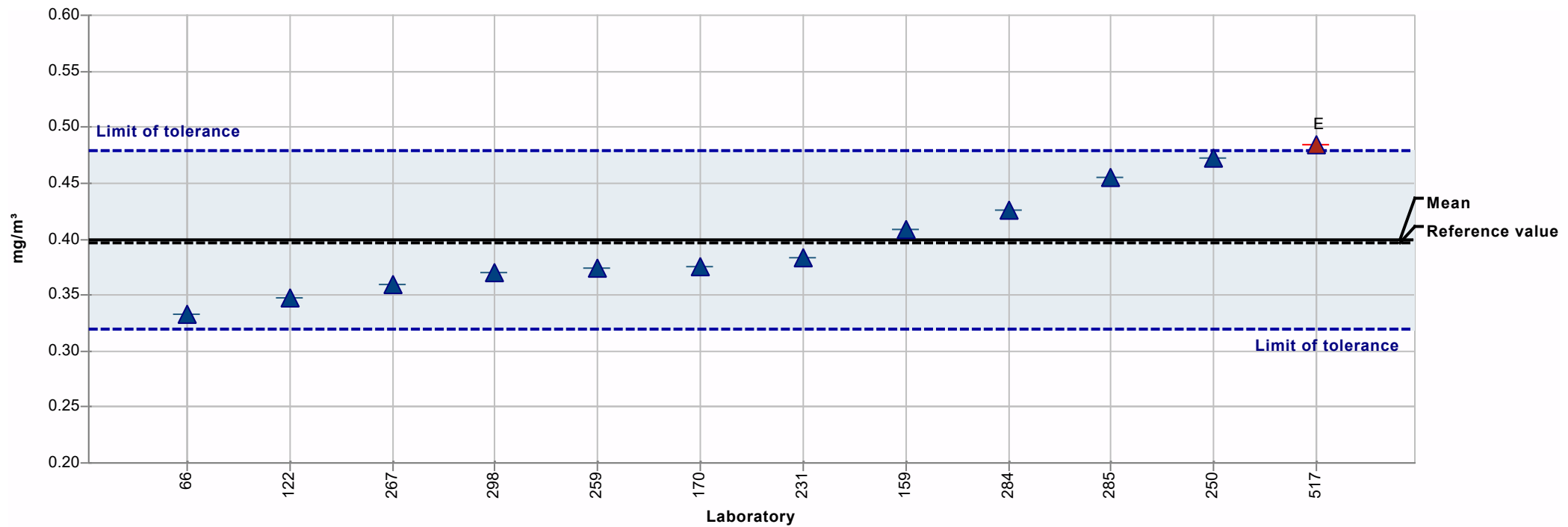
Summary results

Sample:	2	Mean:	0.997 mg/m³
Measurand:	Acetaldehyde	Reproducibility s.d.:	0.064 mg/m³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	6.40%
Rel. target s.d.:	10.00%	Reference value:	0.982 mg/m³
Number of laboratories in calculation: 12		Range of tolerance:	0.798 - 1.197 mg/m³ (Z-Score <= 2.00)



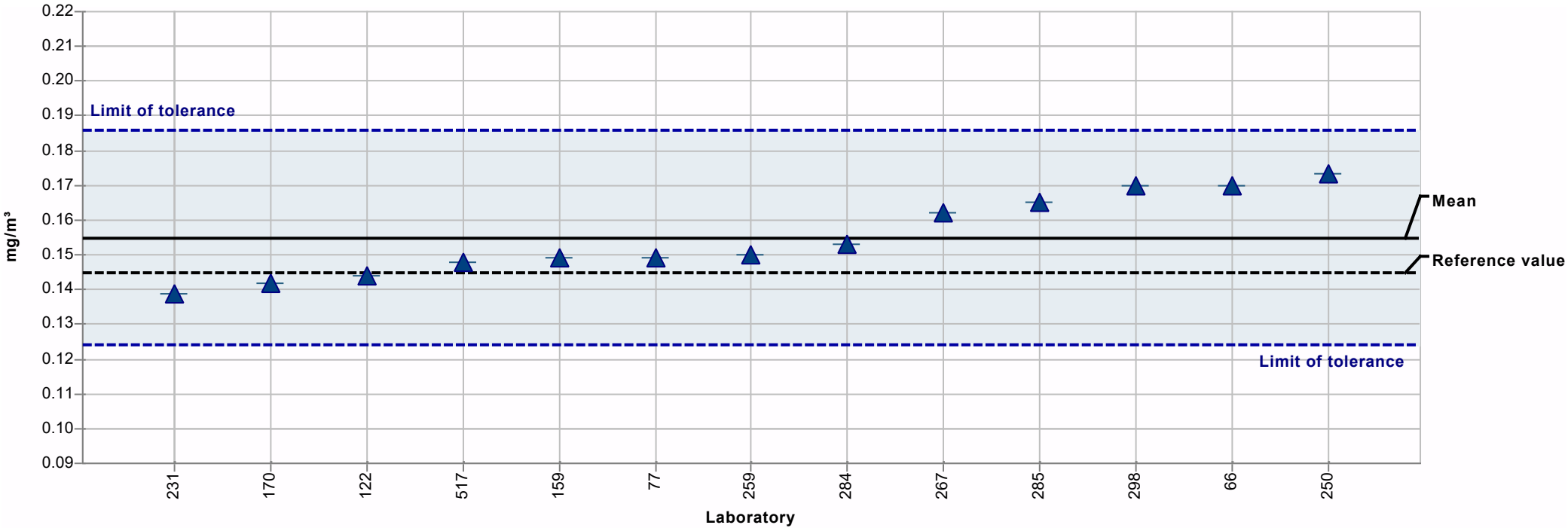
Summary results

Sample:	2	Mean:	0.399 mg/m³
Measurand:	Butyraldehyde	Reproducibility s.d.:	0.050 mg/m³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	12.55%
Rel. target s.d.:	10.00%	Reference value:	0.397 mg/m³
Number of laboratories in calculation: 12		Range of tolerance:	0.319 - 0.479 mg/m³ (Z-Score <= 2.00)



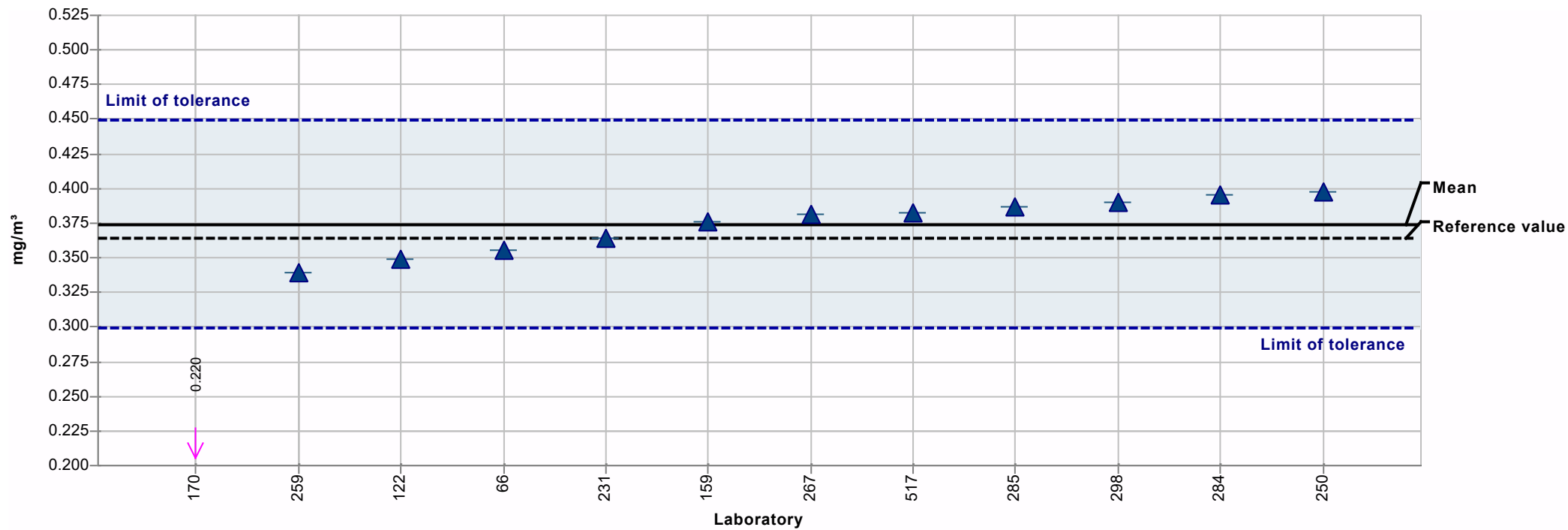
Summary results

Sample:	2	Mean:	0.155 mg/m³
Measurand:	Formaldehyde	Reproducibility s.d.:	0.012 mg/m³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	7.51%
Rel. target s.d.:	10.00%	Reference value:	0.145 mg/m³
Number of laboratories in calculation: 13		Range of tolerance:	0.124 - 0.186 mg/m³ (Z-Score <= 2.00)



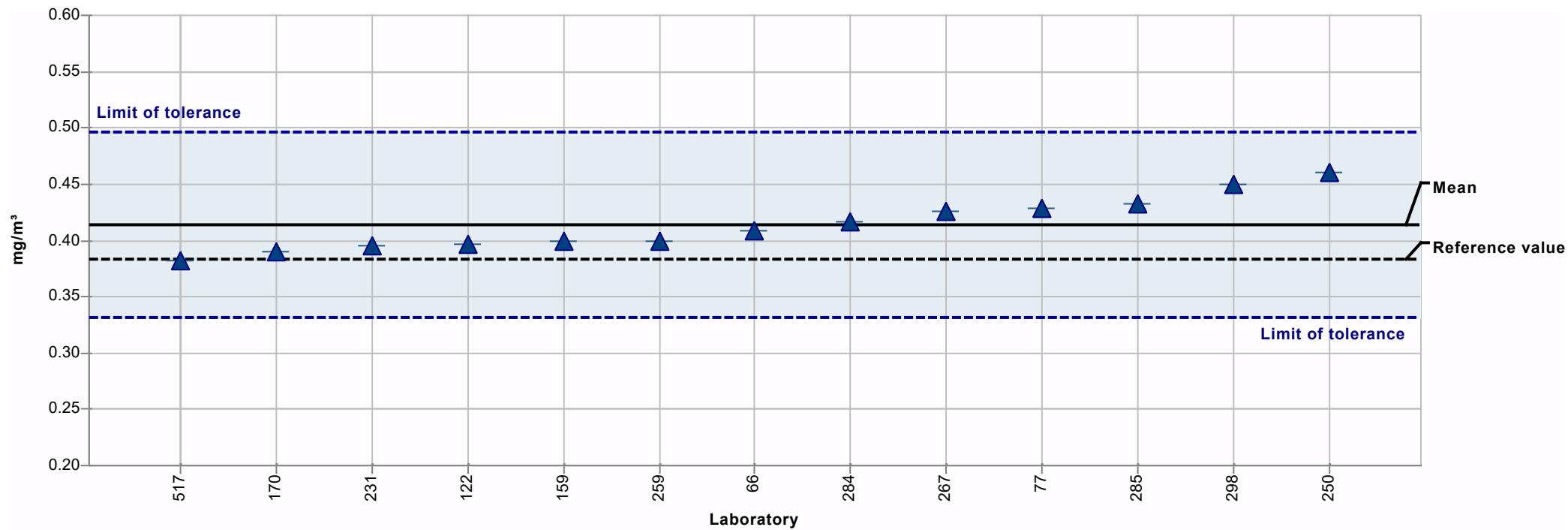
Summary results

Sample:	3	Mean:	0.374 mg/m³
Measurand:	Acetaldehyde	Reproducibility s.d.:	0.020 mg/m³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	5.27%
Rel. target s.d.:	10.00%	Reference value:	0.364 mg/m³
Number of laboratories in calculation: 11		Range of tolerance:	0.299 - 0.449 mg/m³ (Z-Score <= 2.00)



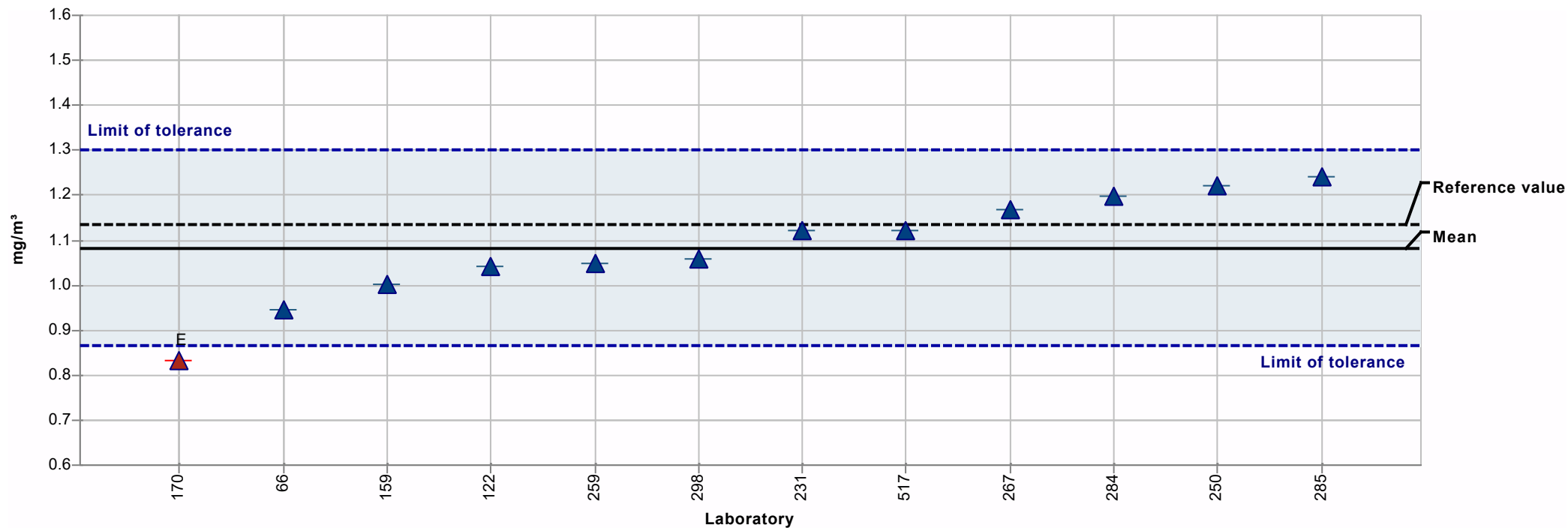
Summary results

Sample:	3	Mean:	0.414 mg/m³
Measurand:	Formaldehyde	Reproducibility s.d.:	0.024 mg/m³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	5.75%
Rel. target s.d.:	10.00%	Reference value:	0.384 mg/m³
Number of laboratories in calculation: 13		Range of tolerance:	0.331 - 0.497 mg/m³ (Z-Score <= 2.00)



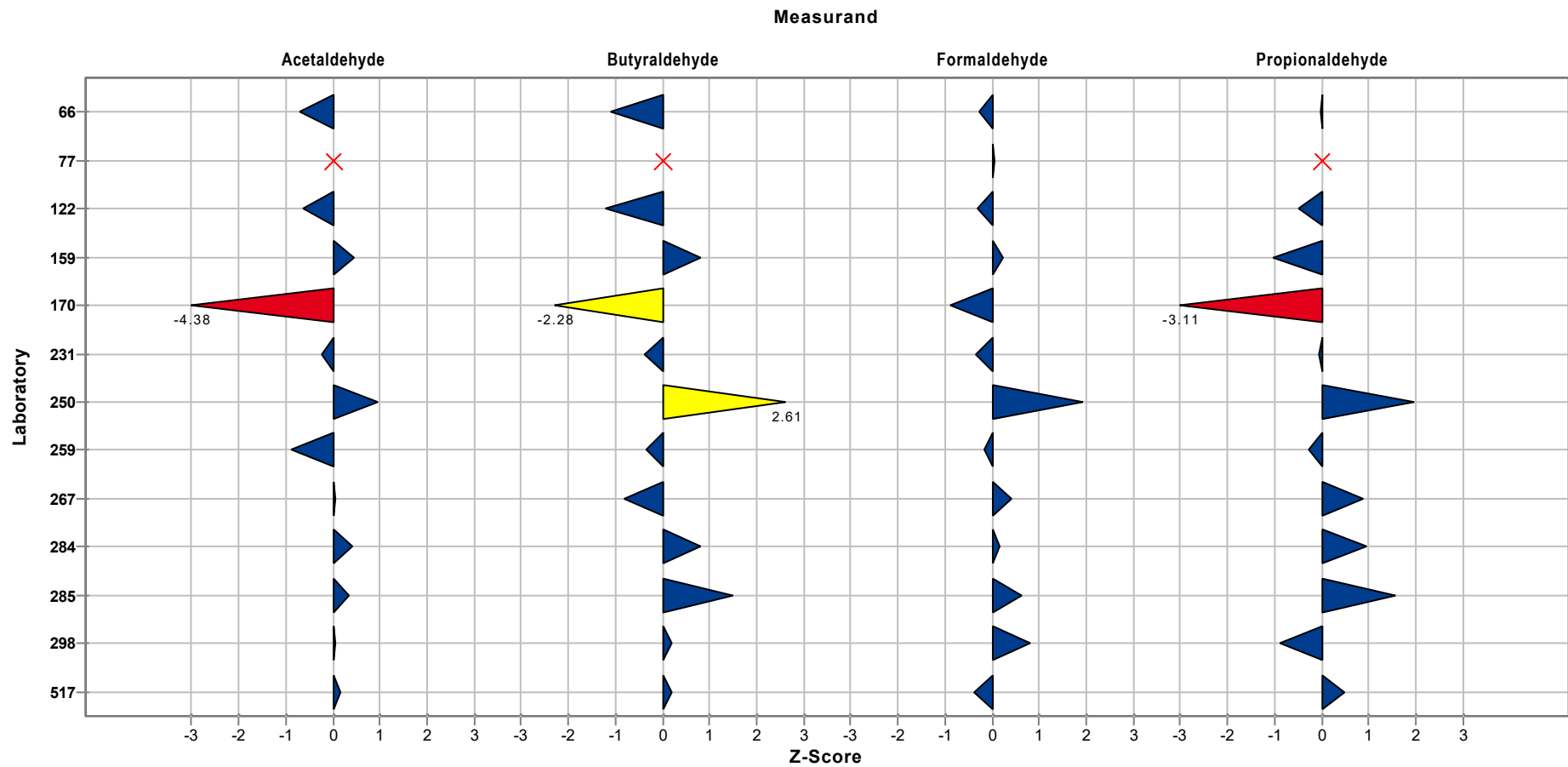
Summary results

Sample:	3	Mean:	1.08 mg/m³
Measurand:	Propionaldehyde	Reproducibility s.d.:	0.12 mg/m³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	11.13%
Rel. target s.d.:	10.00%	Reference value:	1.13 mg/m³
Number of laboratories in calculation:	12	Range of tolerance:	0.87 - 1.30 mg/m³ (Z-Score <= 2.00)



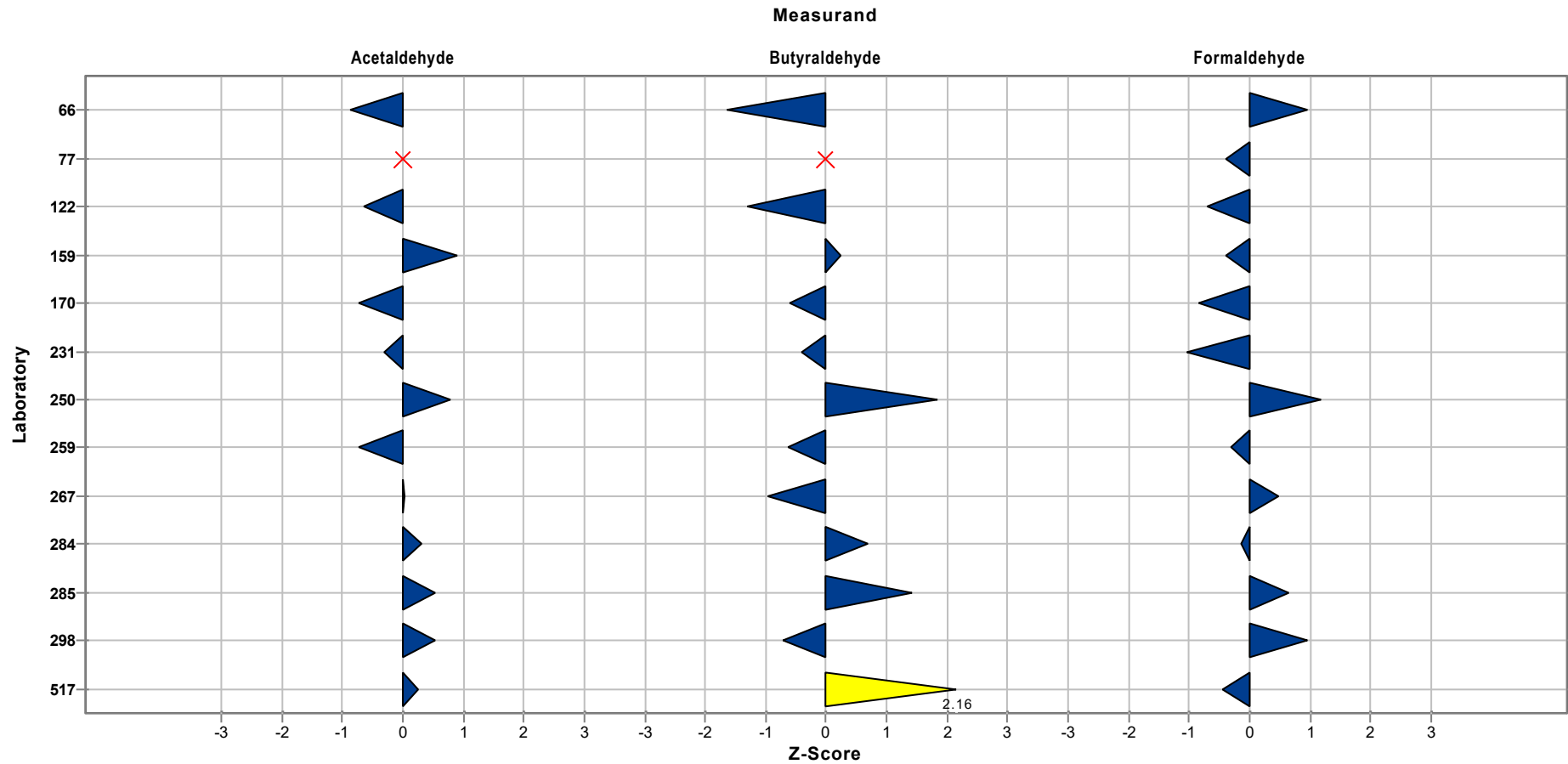
Sample chart of Z-Scores

Sample: 1



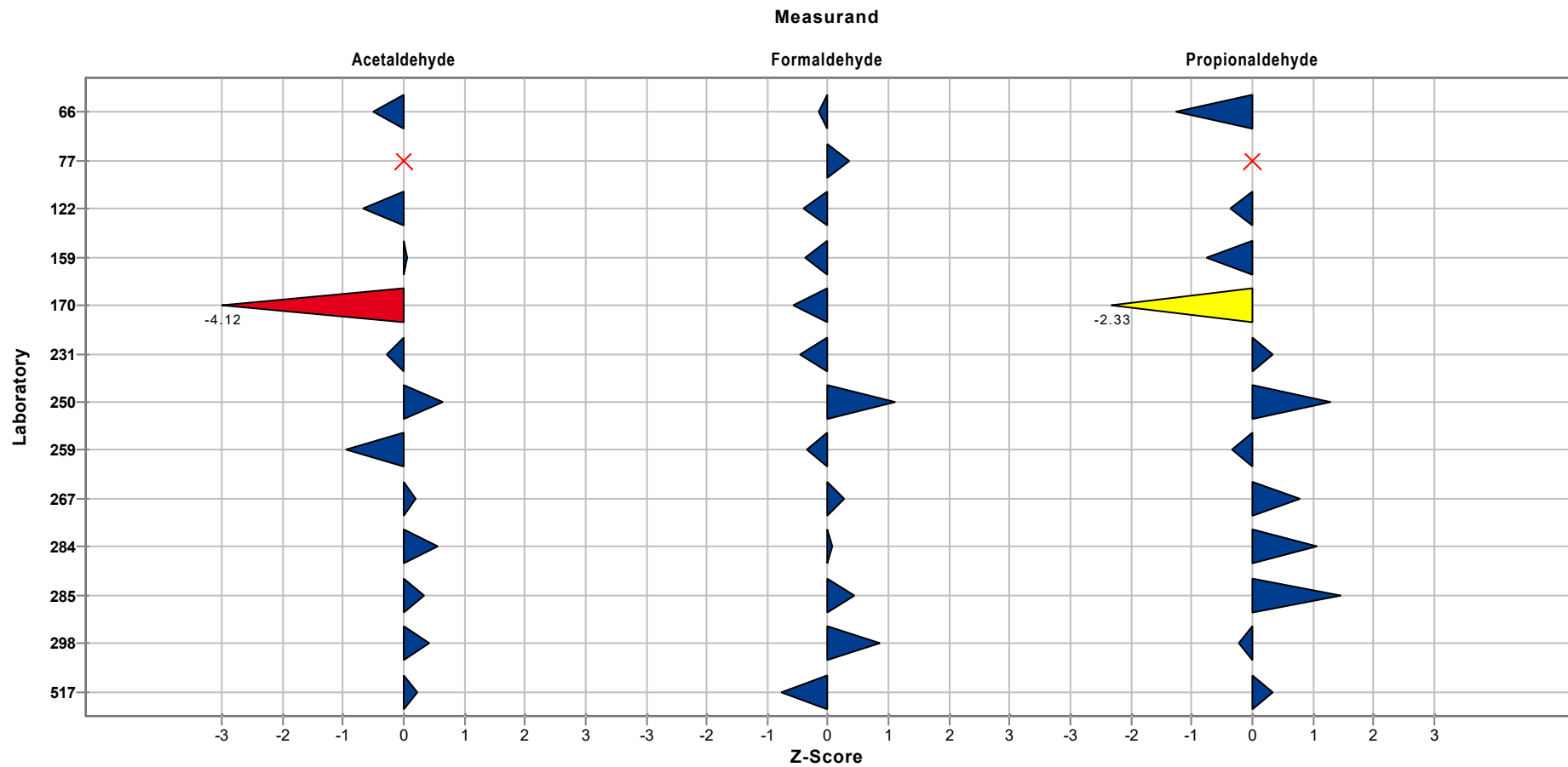
Sample chart of Z-Scores

Sample: 2



Sample chart of Z-Scores

Sample: 3



Questions and Answers

Participant	Type of sample carrier	Sampling pump	Flow rate sampling
66	DNPH-Röhrchen	GSA SG 350	330 - 345 m³/min
77	LpDNPH S10	Gilian GilAir Plus	1000 ml/min
122	DNPH	Gil Air 2 Plus	1200 ml/min
159	Sep-Pak-XPoSure-Kartusche	GSA SG4000	1,0 l/min
170	LpDNPH S10L Cartrige	GilAir Plus	1000ml/min
231	Waters XPosure	GilAir Plus von Sensidyne	0,33 l/min
250	Supelco Lp-DNPH-Kartuschen	Holbach BIVOC 2 (Umweltanalytik Holbach GmbH)	1 L/min
259	Supelco S10 21026-U	Gilian 5000, Gilian GilAir Plus	0,33 l/min; 1,00 l/min; 1,33 l/min
267	DNPH cartridge, Supelco	Gilian GilAir Plus	1L/min
284	Supelco LpDNPH S10	Desaga GS 312	1,0 L/Min
285	DNPH Probenträger	SKC Universal-Probenpumpe 224-PCXR8	0,5 bis 0,6 L/min
298	Supelco LpDNPH S10L	SKC Sampler, Model 224-PCXR8	1 l/min
517	DNPH-Kartusche	GilAir plus	323-341 ml/min

Participant	Flow rate measurement	Sampling time
66	Strömungsmesser Analyt-MTC	120 Minuten
77	TSI 4146F	60 min
122	Defender 520 Medium Flow APMC-370 GPT	60 min
159	Kolbenhubmessgerät Defender 510-H	2h, 1h, 30min
170	BIOS-Defender	120 min
231	TSI 4100	120 Minuten
250	Automatische Volumenstromregelung der Pumpe. Rückführung erfolgt mit Hilfe von DAkKS-kalibrierten Durchflussmessgeräten.	50 min
259	Primärkalibrator 4146 des Herstellers TSI (Thermischer Massenflusssensor)	120 min; 60 min; 15 min
267	Gilibrator 3 (GilAir)	25 min
284	keines	30 Minuten
285	Mesalab Defender 510M	60, 80 und 90 Minuten
298	DryCal	100 Minuten
517	Durchflussmesser Analyt-MTC	120 Minuten

Aldehydes 2024 with own sampling 2

Participant	Analytical method	Date start sample preparation
66	HPLC-DAD nach Derivatisierung und Desorption	19.11.2024
77	DIN ISO 16000-3	
122	DIN EN ISO 16000-3:2023-12	unmittelbar nach der jeweiligen Probenahme (13.11 bzw. 14.11)
159	interne-Methode	18.11.2024
170	DIN ISO 16000-3	21.11.2024
231	IFA Arbeitsmappe 6045 (12/2023)	15.11.2024
250	DIN ISO 16000-3 (2023-12)	18.11.2024
259	DIN ISO 16000-3:2013	21.11.2024
267	ISO 16000-3	18.11.2024
284	DIN ISO 16000-3	13.11.24 (Probe 1); 14.11.2024 (Proben 2 und 3)
285	DIN EN 16000-3 (2023-12)	26.11.2024
298	IFA 6045	
517	HPLC/DAD	19.11.2024

Participant	Storage time after sample prep
66	Kühlschrank
122	Kühlschrank bis Versand an das Labor am 18.11.
159	48h bei RT
170	2h Kühlschrank
231	3 Tage im Kühlschrank
250	k.A.
259	Kühlschrank
267	Analyse direkt nach der Desorption, Analyse der Verdünnungen 15 Tage später (Lagerung der Extrakte im Kühlschrank)
284	DNPH-Kartuschen aus Probe 1: 4 Tage im Kühlschrank, 1 Tag in Kühlbox (Transport), 1 Tag ungekühlt (Versand an Labor); DNPH-Kartuschen aus Proben 2 und 3: 3 Tage im Kühlschrank, 1 Tag in Kühlbox (Transport), 1 Tag ungekühlt (Versand an Labor)
285	nein
517	Kühlschrank

Participant	Date of analysis	Desorption solution	Volume of desorption solution	Chromatography system (HPLC)	Flow rate HPLC
122	19.11.24 - 02.12.2024	Acetonitril			
159	20.11. bis 02.12.2024	2,4-DNPH-Lösung	5ml	Agilent 1100 und 1200	0,8ml/min

Aldehydes 2024 with own sampling 2

Participant	Date of analysis	Desorption solution	Volume of desorption solution	Chromatography system (HPLC)	Flow rate HPLC
170	21.11.2024	Acetonitril	5	Shimadzu Nexera LD-20 , DAD	0,8ml/min
231	18.11.2024 und 19.11.2024	Acetonitril	10 ml	HPLC Dionex Ultimate 3000/UV	0,70 ml/min
250	k.A.	k.A.	k.A.	k.A.	k.A.
259	21.11. und 22.11.2024	Acetonitril	2 ml	LC 2050 (Shimadzu) mit PDA	0,9 ml/min
267	18.11.2024	Acetonitril	5 mL	Agilent HPLC-DAD 1260	1,5 mL/min
284	26.11.2024	Acetonitril	25 ml	Thermo Fisher Scientific, Vanquish Horizon UPLC mit UV-Detektor	0,500 ml/min
285	26.11.2024	Acetonitril	2 mL	Dionex 43000 - Pumpe LPG 3400SD - Detektor DAD-3000 - Sampler WPS-300	1,5 mL/min
517	28.11.2024				

Participant	Mobile phase	Refrigerated autosampler	Analytical column
159	Methanol/Wasser/Acetonitril	nein	ODS- Hypersil 250x 4mm, 5µm der Fa. Hewlett Packard (Agilent)
170	Acetonitril / Wasser	20°C	Restek Allure AK 5 µm 200 * 4,6 mm
231	Acetonitril	nein	SEPSERV UltraSep ES PAH
250	k.A.	k.A.	k.A.
259	A: ACN B: 15% THF in Wasser	15 °C	Nucleosil C18 AB 250 mm x 4 mm; 5 µm
267	Acetonitril/Wasser	Nein, Raumtemperatur	Waters Symmetry C18, 250 mm x 4,6 mm x 5 µm
284	A: 60 % Acetonitril / 40 % Wasser (v/v) B: 95 % Acetonitril / 5 % Wasser (v/v)	Ja, 10°C	Dr.Maisch Grace Grom-Sil ods-5 (200 x 3,0 mm, 3,0 µm) Art. GSOD50312s2003
285	Gradient ACN:H2O 60:40 --> 100:0	nein	Restek Allure AK 5µm 200x4,6 mm

Participant	Column temperature	Wavelength
159	26°C	365nm
170	30°C	365nm
231	40°C	365 nm
250	k.A.	k.A.
259	42 °C	365 nm
267	25 °C	365 nm
284	40 °C	360 nm
285	30 °C	360 nm

Aldehydes 2024 with own sampling 2

Participant	Calibration standard
159	Carbonyl—DNPH Mix 2 Fa. Supelco
170	Fertiger Mix, Sigma-Aldrich, Art. CRM47285
231	Mischstandard von AccuStandard; Kontrollstandard von Neochema
250	k.A.
259	DNPH-Mix 4 Neochema, c = 10 ng/µl für Formaldehyd und Acetaldehyd. Für Propanal und Butanal wurden selbst hergestellte Einzelstandards verwendet: c = 100 ng/µl
267	Fertigmischung von Supelco
284	Fertiger Mix, Sigma-Aldrich, Art. CRM47285
285	Kal: Supelco CRM 47651; Kontrolle: SUPelco CRM 47671; Restek Carb1004 Aldehyde/Ketone (33093)

Participant	Recovery rate
159	ja
170	ja
231	Nein
250	k.A.
259	Die Kartuschen waren nach der Elution farblos (weiß), d.h. die Wiederfindungsrate beträgt 100 %.
267	Nein
284	Nicht anwendbar, da keine Wiederfindungsproben möglich über Kartuschen.
285	nein