

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

Proficiency testing scheme aldehydes with own sampling

16 - 17 October 2018

Summary of laboratory test results

Sample 1

	Acetaldehyde	Z score	Butyraldehyde	Z score	Formaldehyde	Z score
Unit	mg/m ³		mg/m ³		mg/m ³	
2	1,126	-0,60	0,283	-0,14	0,157	-0,74
23	1,166	-0,26	0,282	-0,17	0,170	0,02
33	1,297	0,83	0,273	-0,49	0,184	0,87
97	1,168	-0,25	0,288	0,03	0,164	-0,33
159	1,316	0,99	0,303	0,56	0,161	-0,51
171	1,020	-1,48	0,256	-1,08	0,155	-0,86
175	1,070	-1,06	0,290	0,10	0,150	-1,16
184	1,220	0,19	0,277	-0,35	0,164	-0,33
230	1,240	0,36	0,324	1,29	0,180	0,61
236	1,195	-0,02	0,277	-0,35	0,163	-0,39
265	1,349	1,27	0,286	-0,03	0,170	0,02
285	1,230	0,27	0,330	1,50	0,190	1,20
291	1,130	-0,56			0,210	2,38 E
508	1,236	0,32	0,262	-0,87	0,156	-0,80
-	-	--	-	--	-	--
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	14		13		14	
Mean	1,197		0,287		0,170	
Reproducibility s.d.	0,092		0,021		0,016	
Rel. reproducibility s.d.	7,72 %		7,46 %		9,67 %	
Reference value	1,139		0,283		0,150	
Target s.d.	0,120		0,029		0,017	
Rel. target s.d.	10,00 %		10,00 %		10,00 %	
Lower limit of tolerance	0,958		0,230		0,136	
Upper limit of tolerance	1,437		0,344		0,204	
No. of laboratories after elimination of outliers type A-D and F (without)	14		13		14	

	Acetaldehyde	Z score	Butyraldehyde	Z score	Formaldehyde	Z score
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\text{-Score} > 3,5$						

Summary of laboratory test results

Sample 2

	Acetaldehyde	Z score	Butyraldehyde	Z score	Formaldehyde	Z score
Unit	mg/m ³		mg/m ³		mg/m ³	
2	0,959	-0,67	1,067	-0,06	0,066	-0,36
23	0,966	-0,60	1,003	-0,65	0,070	0,22
33	1,069	0,40	0,976	-0,90	0,084	2,23 E
97	0,989	-0,37	1,107	0,32	0,065	-0,51
159	1,107	0,77	1,122	0,46	0,068	-0,07
171	0,755	-2,65 BE	0,980	-0,87	0,067	-0,17
175	0,910	-1,14	1,120	0,44	0,060	-1,24
184	1,030	0,02	1,035	-0,35	0,069	0,03
230	1,090	0,61	1,220	1,37	0,072	0,51
236	1,018	-0,09	1,085	0,11	0,062	-0,93
265	1,133	1,03	1,069	-0,04	0,067	-0,22
285	1,010	-0,17	1,200	1,18	0,082	1,97
291	1,050	0,22			0,066	-0,36
508	1,027	-0,01	0,965	-1,01	0,061	-1,09
-	-	--	-	--	-	--
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	14		13		14	
Mean	1,028		1,073		0,068	
Reproducibility s.d.	0,063		0,082		0,007	
Rel. reproducibility s.d.	6,14 %		7,60 %		10,16 %	
Reference value	0,960		1,095		0,058	
Target s.d.	0,103		0,107		0,007	
Rel. target s.d.	10,00 %		10,00 %		10,00 %	
Lower limit of tolerance	0,822		0,858		0,055	
Upper limit of tolerance	1,233		1,288		0,082	
Type B outliers	1					
No. of laboratories after elimination of	13		13		14	

Summary of laboratory test results

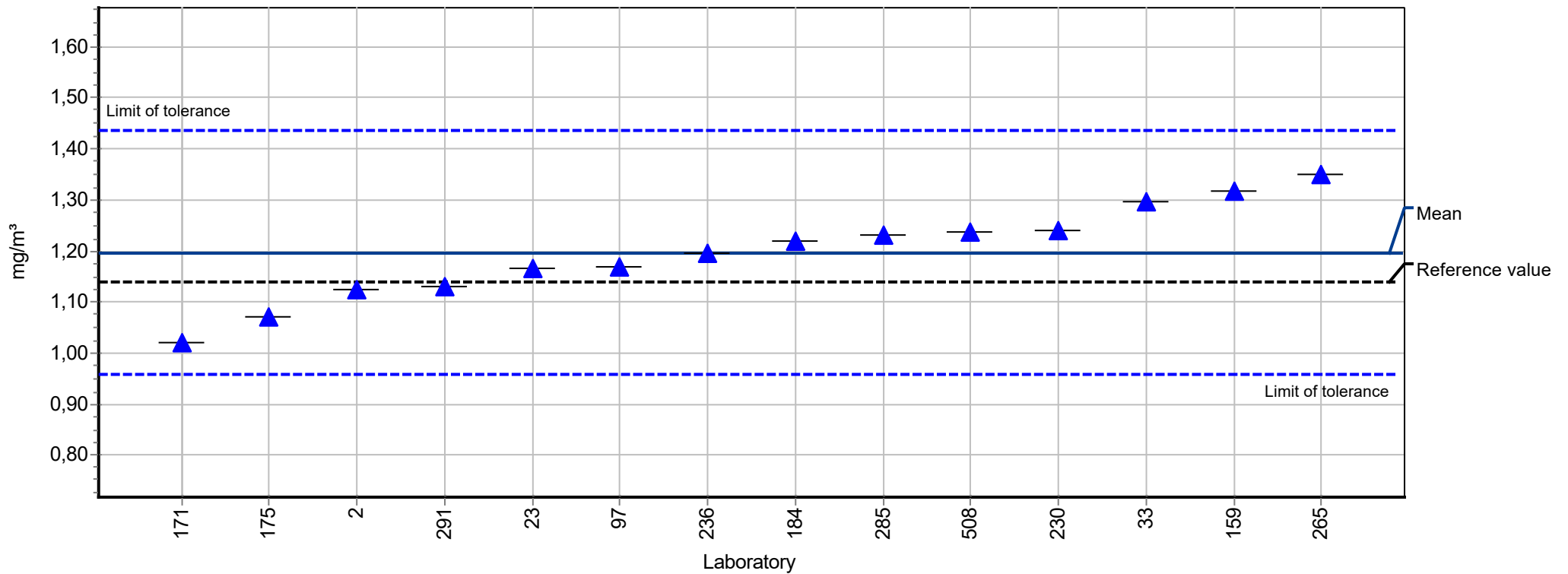
Sample 3

	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	
2	0,404	-0,72	0,899	-0,09	0,122	-0,60	0,755	-0,49
23	0,432	-0,07	0,854	-0,59	0,133	0,25	0,771	-0,31
33	0,447	0,28	0,822	-0,95	0,144	1,07	0,713	-0,98
97	0,419	-0,37	0,952	0,49	0,129	-0,06	0,784	-0,15
159	0,459	0,55	0,945	0,41	0,123	-0,52	0,710	-1,02
171	0,321	-2,62 BE	0,864	-0,48	0,130	0,02	0,675	-1,42
175	0,390	-1,04	0,960	0,58	0,120	-0,75	0,740	-0,67
184	0,425	-0,23	0,868	-0,44	0,129	-0,06	0,764	-0,39
230	0,460	0,57	1,040	1,46	0,135	0,40	0,900	1,20
236	0,432	-0,07	0,838	-0,77	0,127	-0,21	0,935	1,61
265	0,486	1,17	0,913	0,06	0,133	0,25	0,904	1,25
285	0,440	0,11	1,020	1,24	0,146	1,25	0,900	1,20
291	0,425	-0,23			0,127	-0,21		
508	0,438	0,07	0,823	-0,93	0,119	-0,83	0,812	0,17
-	-	--	-	--	-	--	-	--
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	14		13		14		13	
Mean	0,435		0,908		0,130		0,797	
Reproducibility s.d.	0,025		0,072		0,008		0,086	
Rel. reproducibility s.d.	5,72 %		7,93 %		6,19 %		10,76 %	
Reference value	0,397		0,920		0,114		0,749	
Target s.d.	0,044		0,091		0,013		0,086	
Rel. target s.d.	10,00 %		10,00 %		10,00 %		10,76 %	
Lower limit of tolerance	0,348		0,726		0,104		0,626	
Upper limit of tolerance	0,522		1,089		0,156		0,969	
Type B outliers	1							
No. of laboratories after elimination of	13		13		14		13	

	Acetaldehyde	Z score	Butyraldehyde	Z score	Formaldehyde	Z score	Propionaldehyde	Z score
outliers type A-D and F (w ithout 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 >3,5								

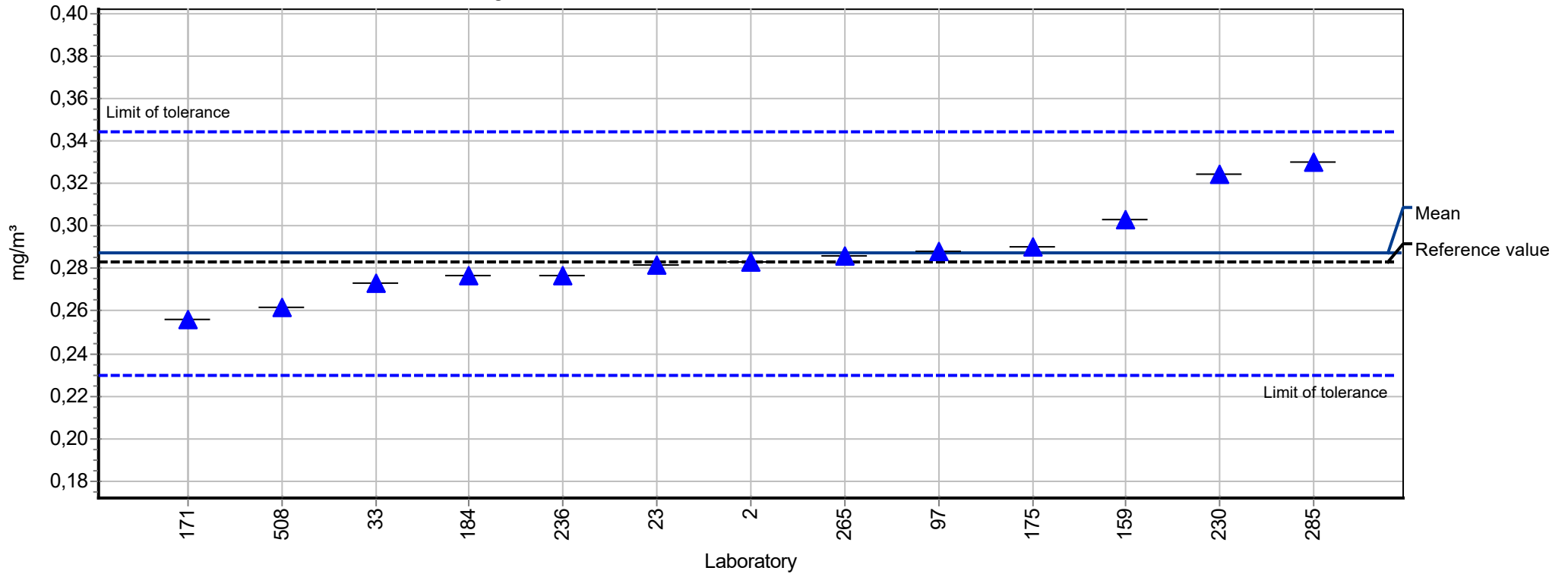
Summary results

Measurand:	Acetaldehyde	Mean:	1,197 mg/m ³
Sample:	1	Reprod. s.d.:	0,092 mg/m ³
Method:	ISO 5725-2	Rel.reprod. s.d.:	7,72%
Rel.target s.d.:	10,00% (Limited)	Reference value:	1,139 mg/m ³
No. of laboratories:	14	Range of tolerance:	0,958 - 1,437 mg/m ³ (Z-Score <= 2,00)



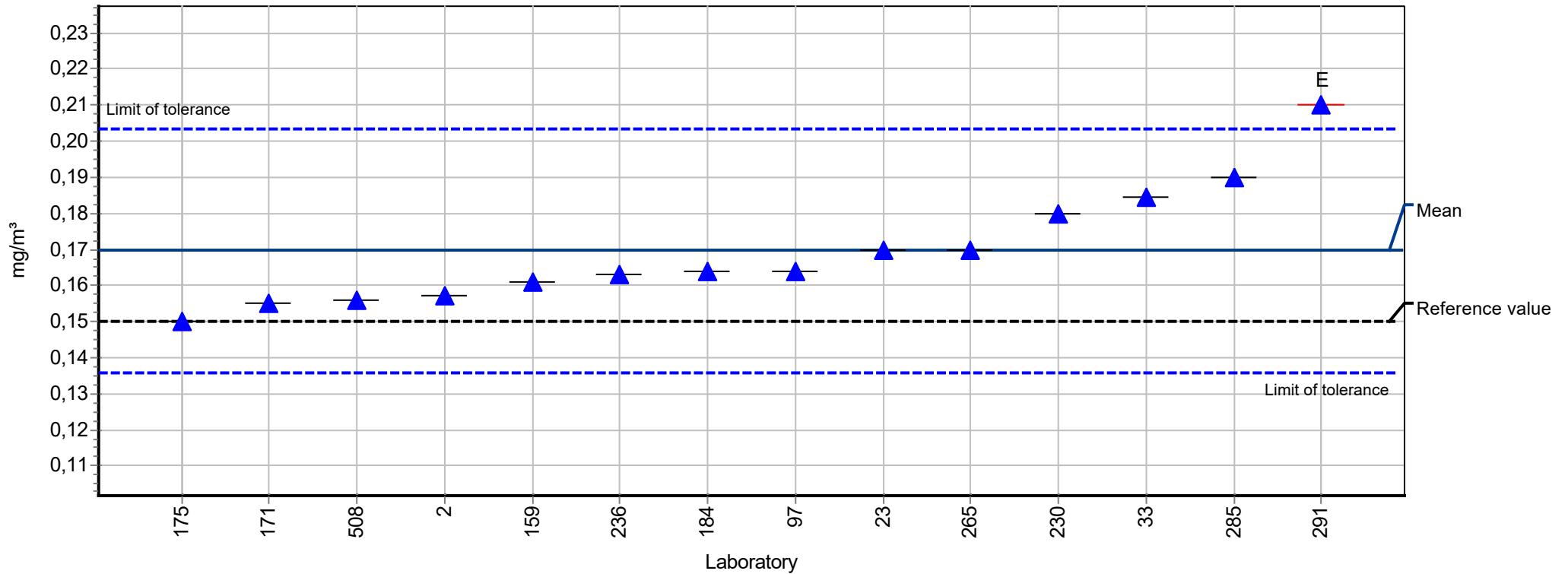
Summary results

Measurand:	Butyraldehyde	Mean:	0,287 mg/m ³
Sample:	1	Reprod. s.d.:	0,021 mg/m ³
Method:	ISO 5725-2	Rel.reprod. s.d.:	7,46%
Rel.target s.d.:	10,00% (Limited)	Reference value:	0,283 mg/m ³
No. of laboratories:	13	Range of tolerance:	0,230 - 0,344 mg/m ³ (Z-Score <= 2,00)



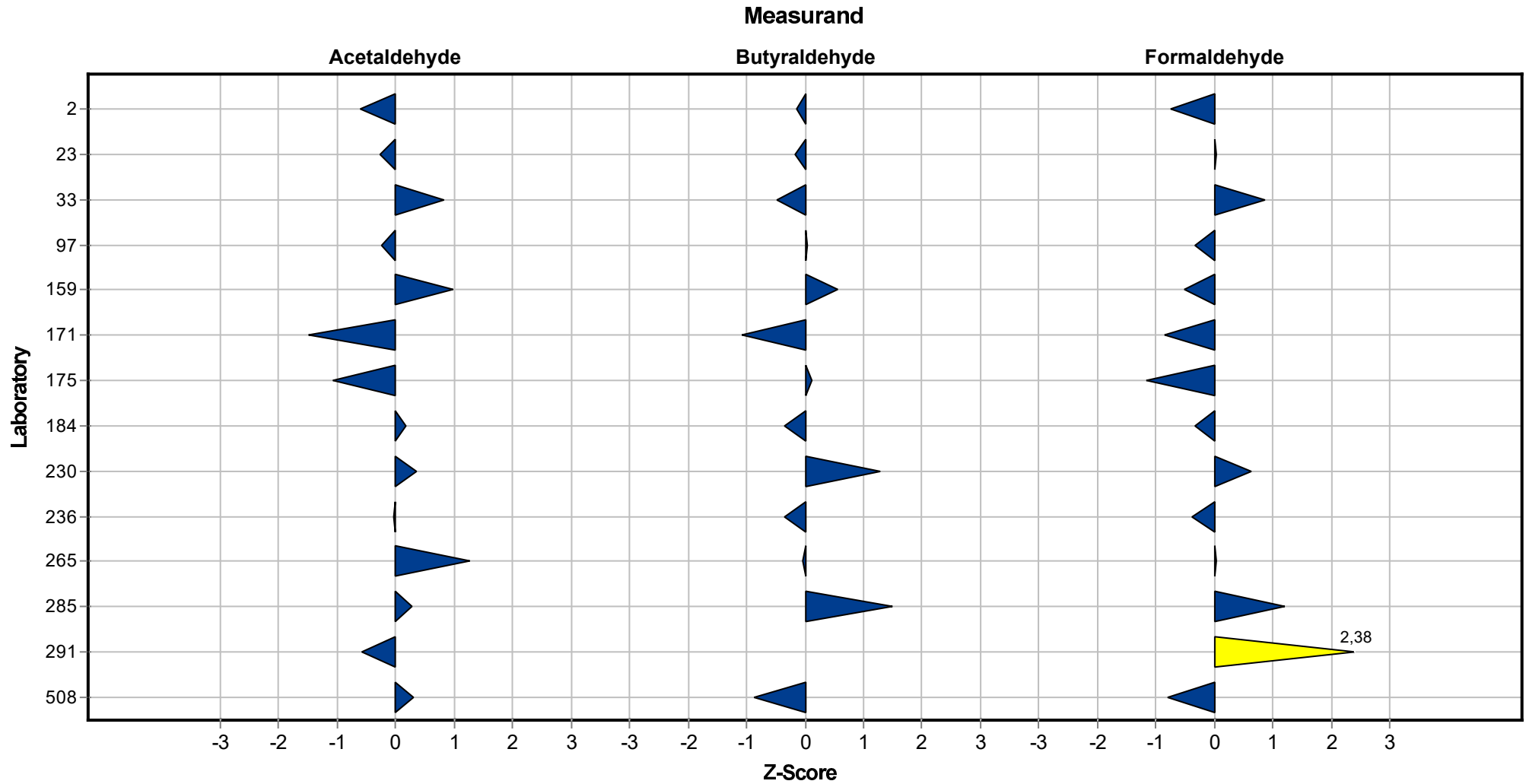
Summary results

Measurand:	Formaldehyde	Mean:	0,170 mg/m ³
Sample:	1	Reprod. s.d.:	0,016 mg/m ³
Method:	ISO 5725-2	Rel.reprod. s.d.:	9,67%
Rel.target s.d.:	10,00% (Limited)	Reference value:	0,150 mg/m ³
No. of laboratories:	14	Range of tolerance:	0,136 - 0,204 mg/m ³ (Z-Score <= 2,00)



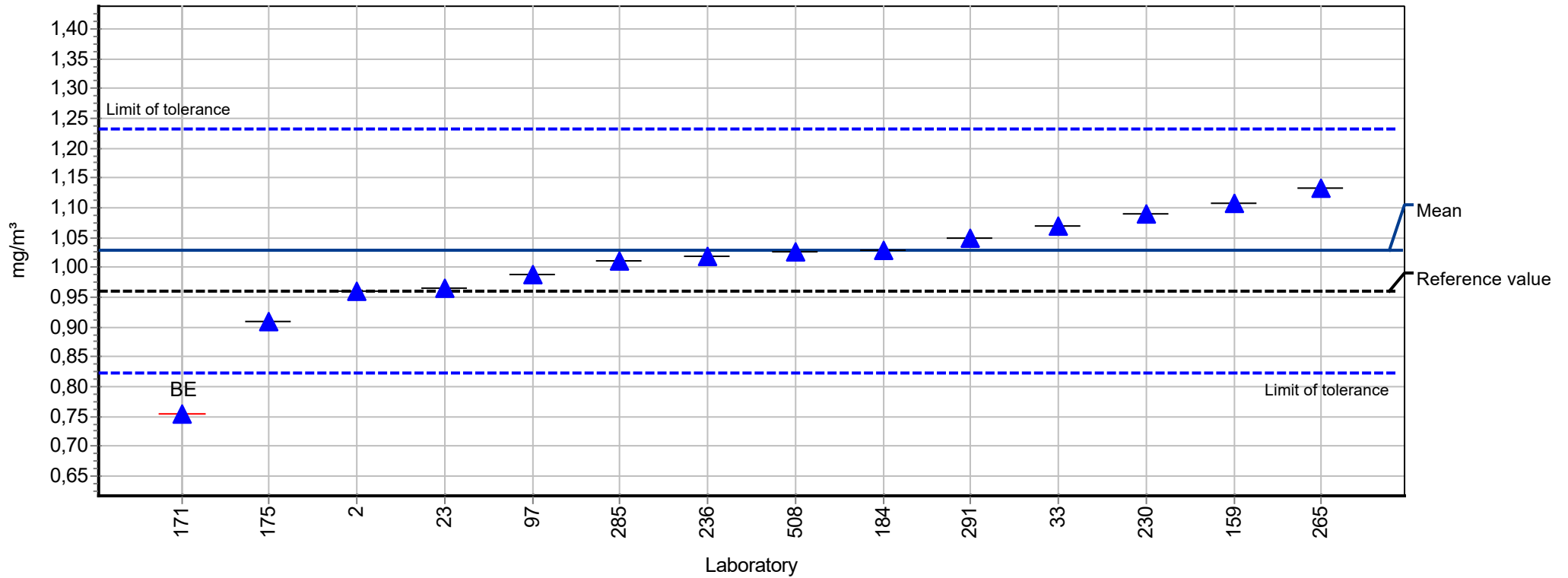
Sample chart of Z-scores

Sample 1



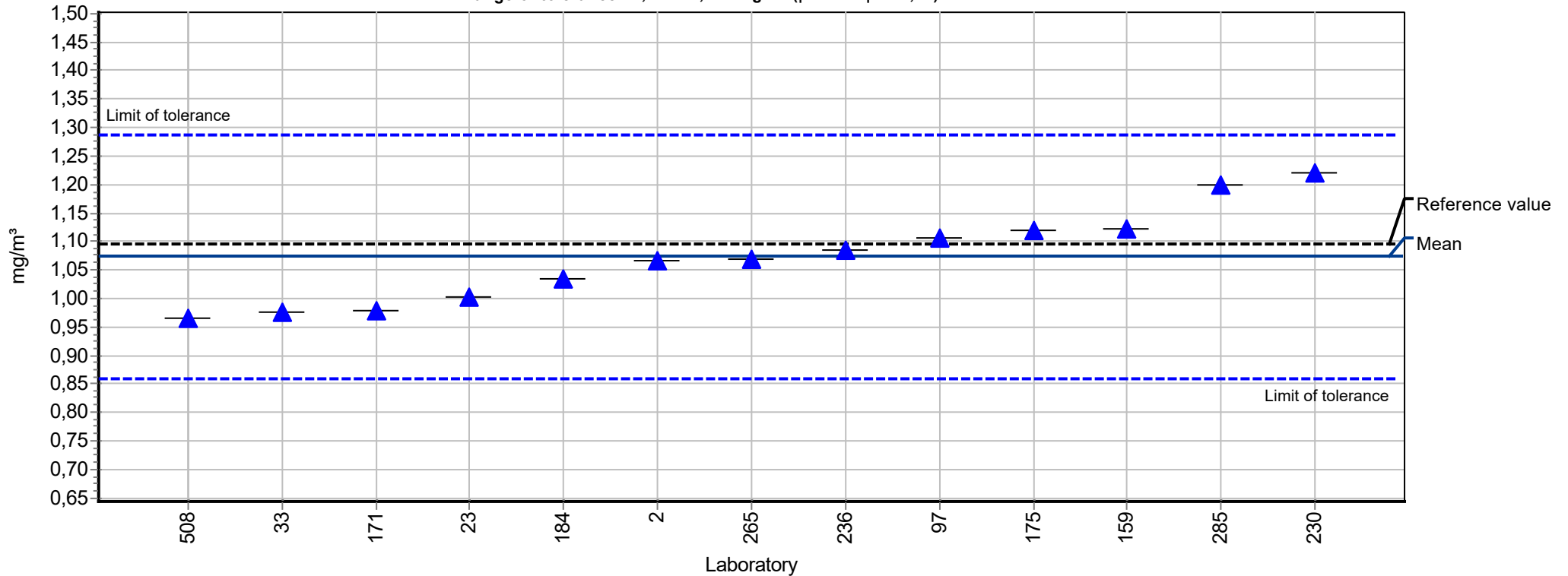
Summary results

Measurand:	Acetaldehyde	Mean:	1,028 mg/m ³
Sample:	2	Reprod. s.d.:	0,063 mg/m ³
Method:	ISO 5725-2	Rel.reprod. s.d.:	6,14%
Rel.target s.d.:	10,00% (Limited)	Reference value:	0,960 mg/m ³
No. of laboratories:	13	Range of tolerance:	0,822 - 1,233 mg/m ³ (Z-Score <= 2,00)



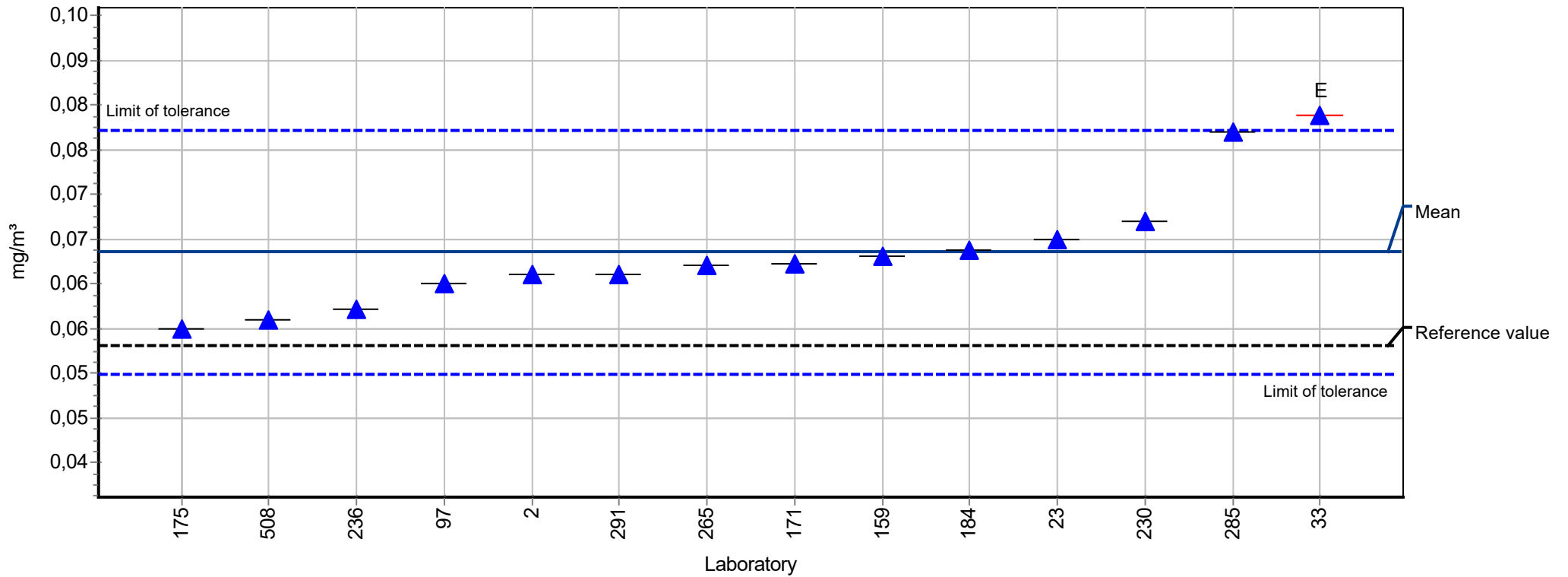
Summary results

Measurand:	Butyraldehyde	Mean:	1,073 mg/m ³
Sample:	2	Reprod. s.d.:	0,082 mg/m ³
Method:	ISO 5725-2	Rel.reprod. s.d.:	7,60%
Rel.target s.d.:	10,00% (Limited)	Reference value:	1,095 mg/m ³
No. of laboratories:	13	Range of tolerance:	0,858 - 1,288 mg/m ³ (Z-Score <= 2,00)



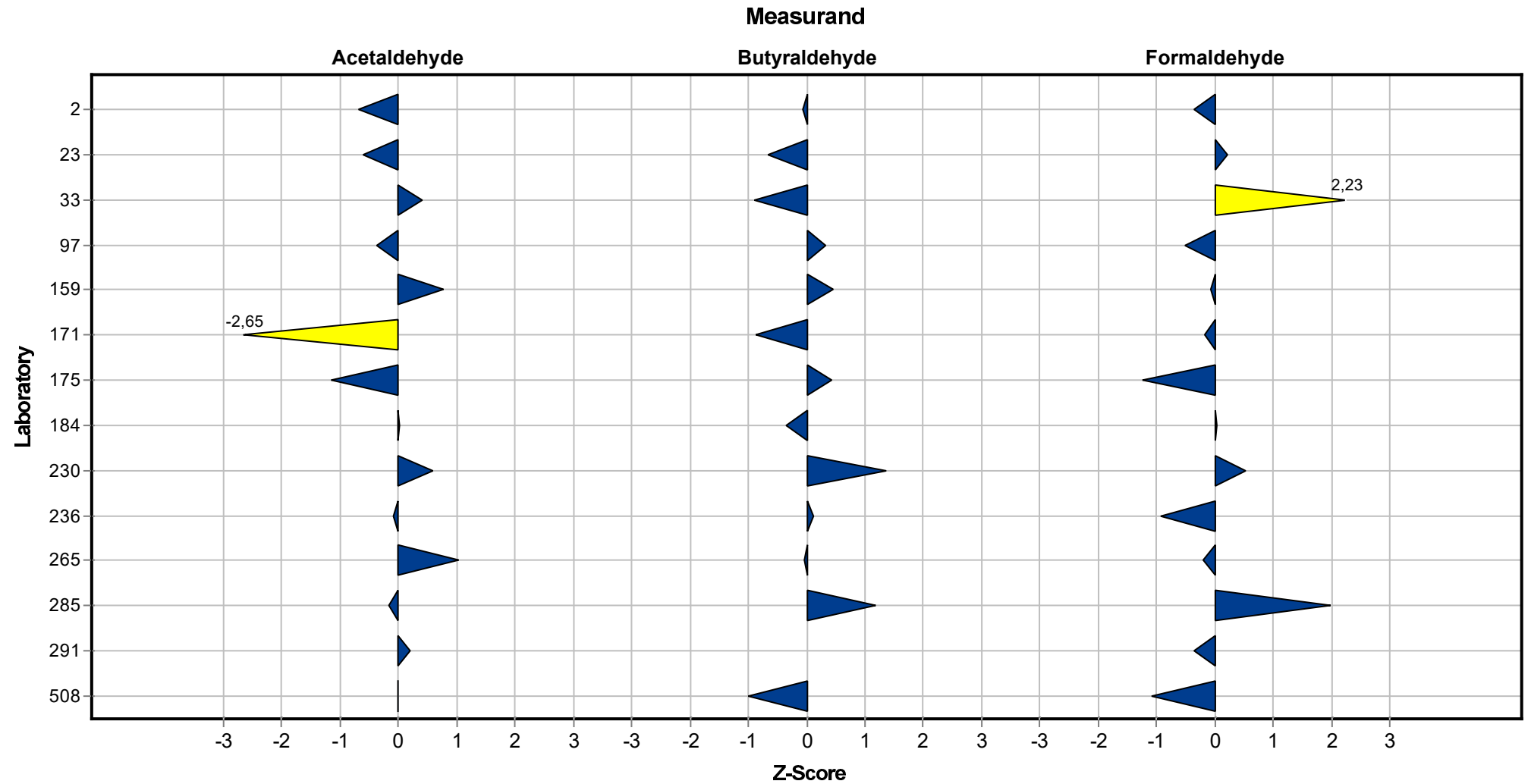
Summary results

Measurand:	Formaldehyde	Mean:	0,068 mg/m ³
Sample:	2	Reprod. s.d.:	0,007 mg/m ³
Method:	ISO 5725-2	Rel.reprod. s.d.:	10,16%
Rel.target s.d.:	10,00% (Limited)	Reference value:	0,058 mg/m ³
No. of laboratories:	14	Range of tolerance:	0,055 - 0,082 mg/m ³ (Z-Score ≤ 2,00)



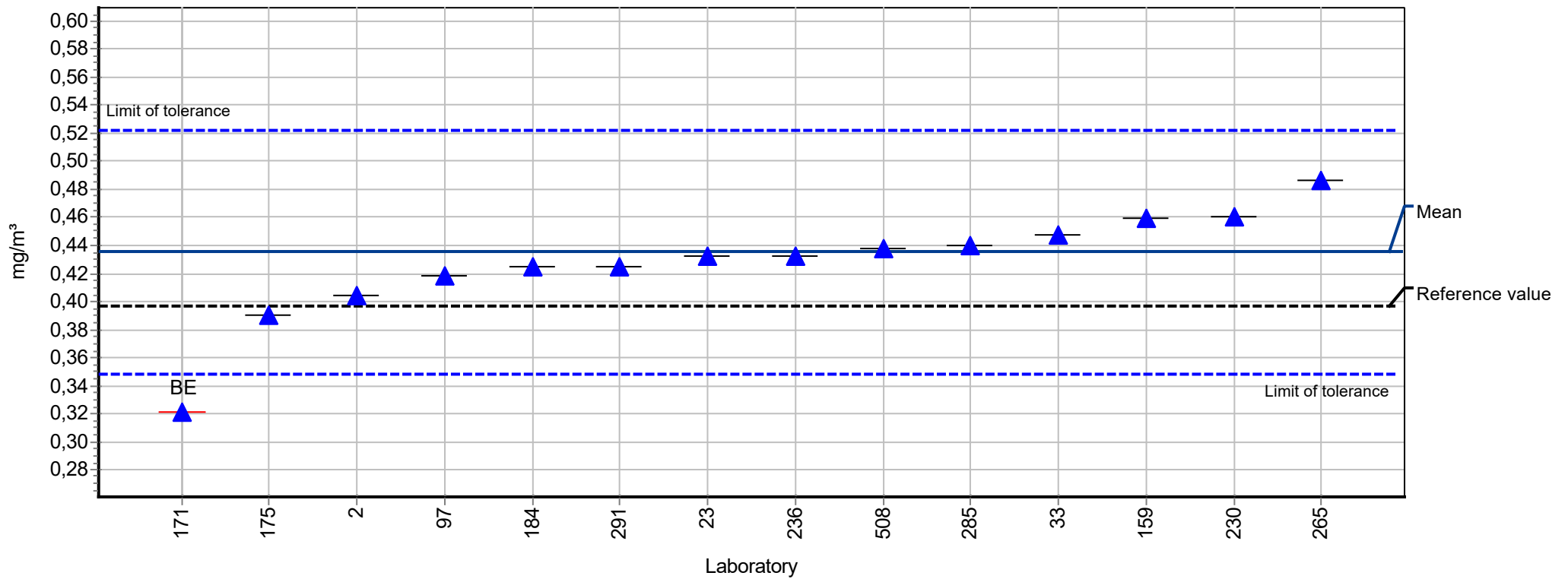
Sample chart of Z-scores

Sample 2



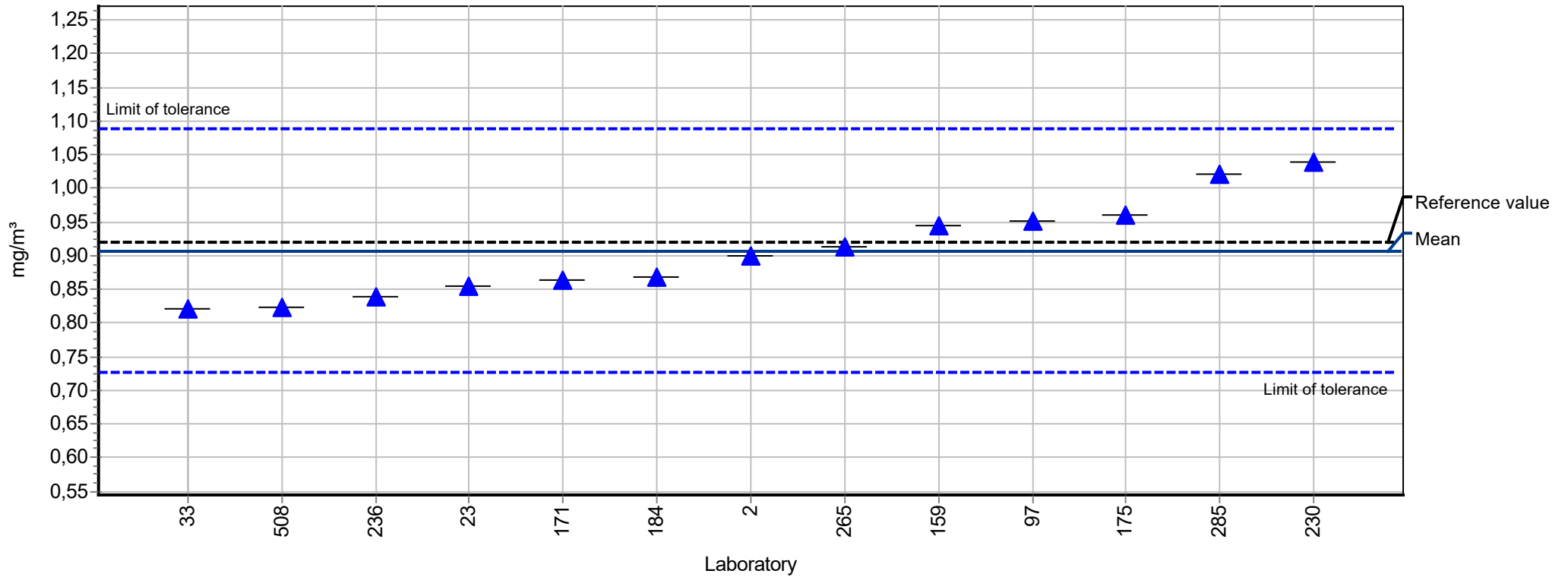
Summary results

Measurand:	Acetaldehyde	Mean:	0,435 mg/m ³
Sample:	3	Reprod. s.d.:	0,025 mg/m ³
Method:	ISO 5725-2	Rel.reprod. s.d.:	5,72%
Rel.target s.d.:	10,00% (Limited)	Reference value:	0,397 mg/m ³
No. of laboratories:	13	Range of tolerance:	0,348 - 0,522 mg/m ³ (Z-Score <= 2,00)



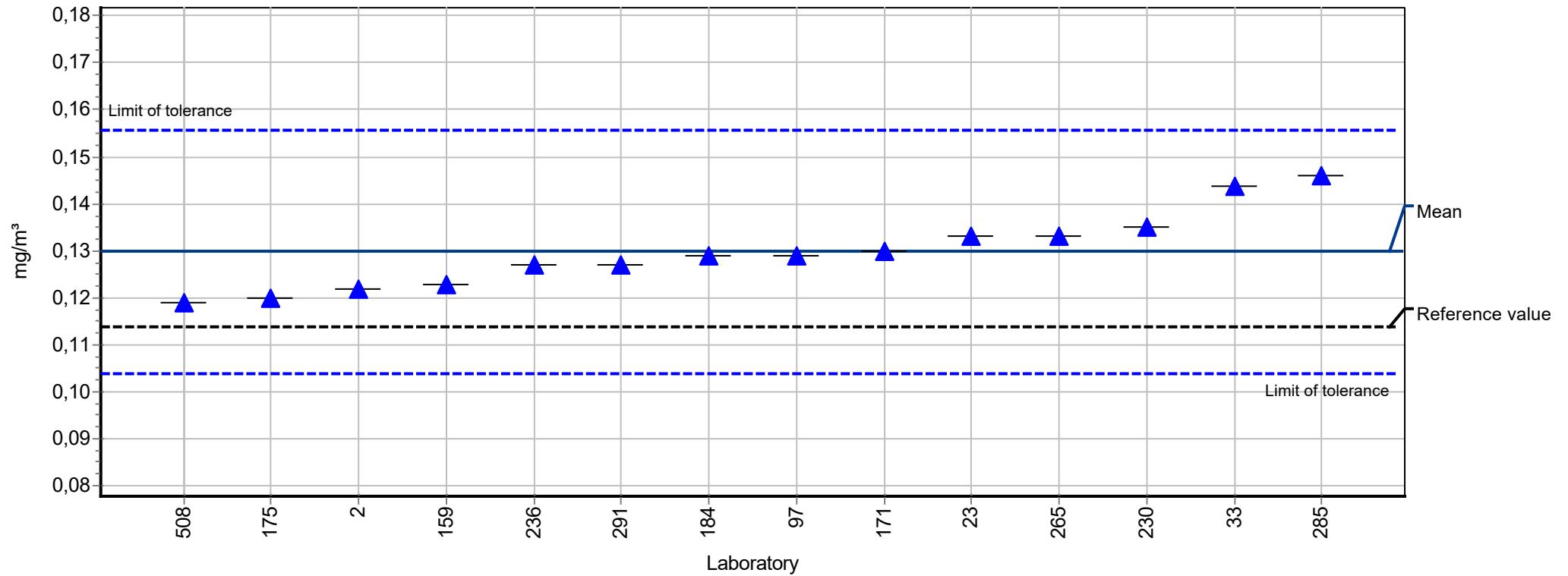
Summary results

Measurand:	Butyraldehyde	Mean:	0,908 mg/m ³
Sample:	3	Reprod. s.d.:	0,072 mg/m ³
Method:	ISO 5725-2	Rel.reprod. s.d.:	7,93%
Rel.target s.d.:	10,00% (Limited)	Reference value:	0,920 mg/m ³
No. of laboratories:	13	Range of tolerance:	0,726 - 1,089 mg/m ³ (Z-Score <= 2,00)



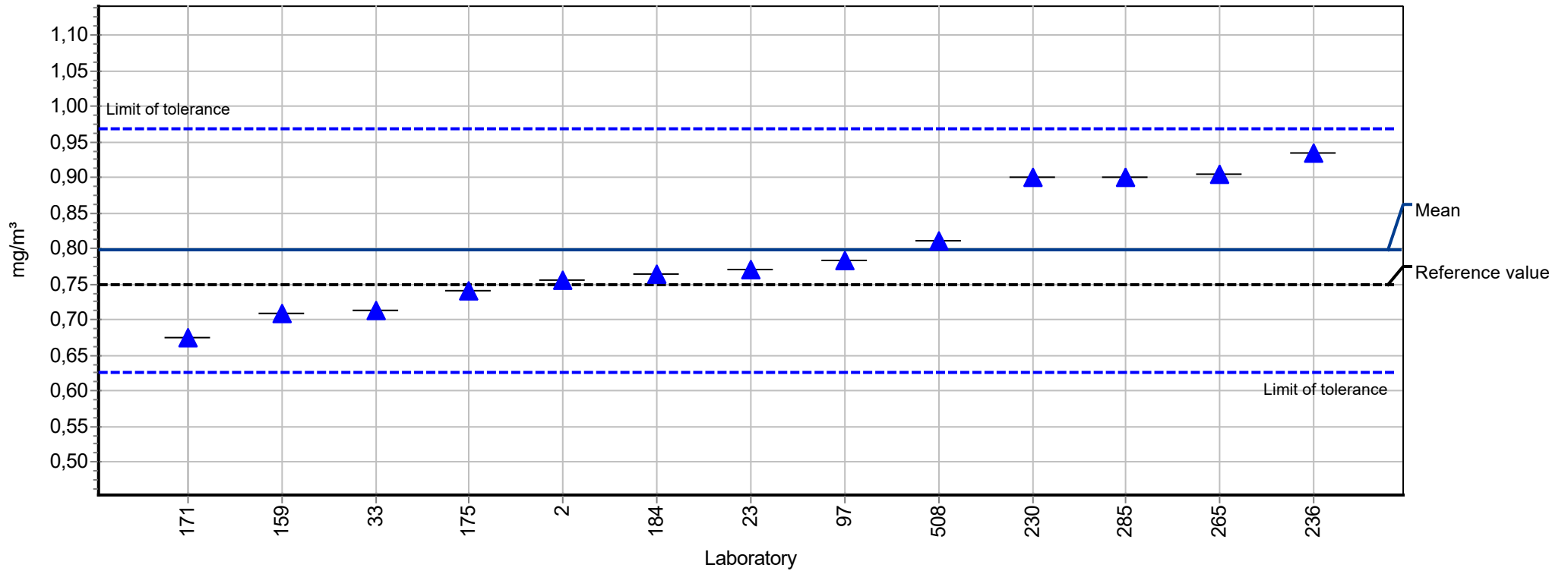
Summary results

Measurand:	Formaldehyde	Mean:	0,130 mg/m ³
Sample:	3	Reprod. s.d.:	0,008 mg/m ³
Method:	ISO 5725-2	Rel.reprod. s.d.:	6,19%
Rel.target s.d.:	10,00% (Limited)	Reference value:	0,114 mg/m ³
No. of laboratories:	14	Range of tolerance:	0,104 - 0,156 mg/m ³ (Z-Score <= 2,00)



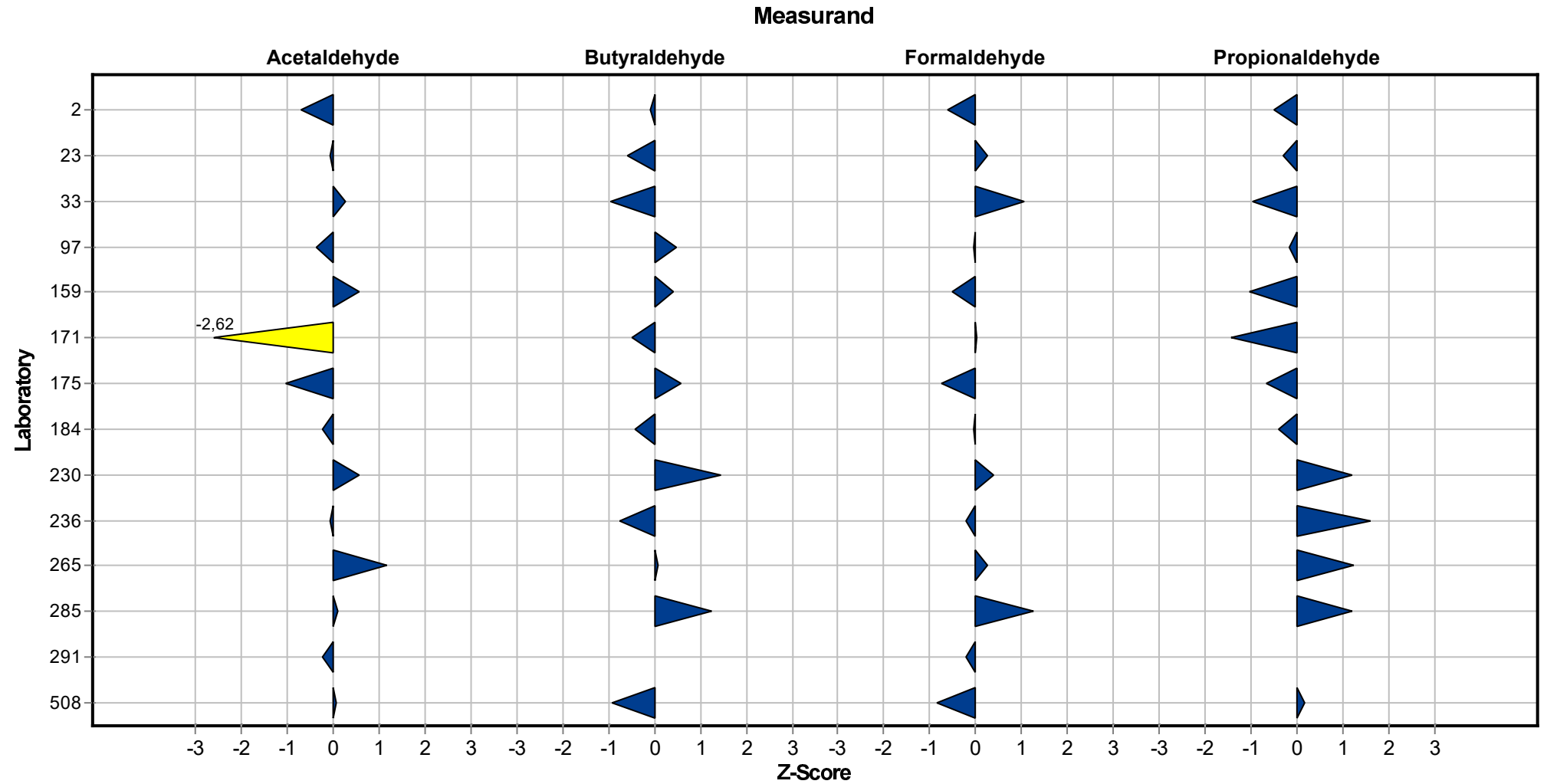
Summary results

Measurand:	Propionaldehyde	Mean:	0,797 mg/m ³
Sample:	3	Reprod. s.d.:	0,086 mg/m ³
Method:	ISO 5725-2	Rel.reprod. s.d.:	10,76%
Rel.target s.d.:	10,76% (Limited)	Reference value:	0,749 mg/m ³
No. of laboratories:	13	Range of tolerance:	0,626 - 0,969 mg/m ³ ($ Z\text{-Score} \leq 2,00$)



Sample chart of Z-scores

Sample 3



Questions and Answers

Participant	Type of sample carrier	Sampling pump	Volume flow
2	LpDNPH S10, Fa. Supelco , No. 21014	Aircheck	1 L/Min.
23	DNPH Kartusche von Supelco	BIVOC 2	800ml/min
33	Waters DNPH Silicagel WAT 039550	SKC Personal Air Sampler 224PCMTX8	0,1; 0,15; 0,2 L/min
97	Supelco S10 DNPH-Kartuschen	BIVOC / SG350ex	1 l/min / 0,333 l/min
159	Waters Sep-Pak XPoSure Aldehyd Sampler	SG 2500ex	1,0 Liter/min
171	LpDNPH S10x Cartridge; Supelco Analytical	Gilian GilAir Plus	2 l/min
175	Water SepPak	GSA 5100, SKC Pocket Pump and SKC Pocket Touch	100, 200, 400, 1000, 1500 ml/min
184	Supelco Lp DNPH S10	Gilan Gilair+; GSA SG 4000	0,24 - 0,26 l/min
230	DNPH, SEP-PAK XPosur, Fa. Waters	Holbach, BIVOC 2	1l/min
236	SKC Röhrrchen Nr. 226-119	Gilian LFS 113	100 ml/min
265	Waters DNPH Kartuschen Shortbody	Desaga GS312	1,0 l/min
285	SKC DNPH coated silica gel	SKC 224-PCXR8	0,33 l/min
291	LP-DNPH-10 Vol. 3ml von Sigma	Honold	1 l/min
508	Waters DNPH Kartuschen Shortbody	Desaga GS312	1,0 l/min

Participant	Volume flow measurement	Sampling time	Analytical method
2	Defender 530	10 Min. und 20 Min.	IFA-Arbeitsmappe Kennzahl 6045
23	BIOS Definer 220 M	62,5min, 125min	i.A. nach ISO 16000-3 (Aldehyde/Ketone)
33	Bios Defender 510	120 min	IFA 6045
97	Defender 510H / Defender 510L	45 Minuten	HPLC
159	DryCal	30 min und 60 min	BGN-Methode 2017-01 2P, HPLC, PN mit DNPH
171	TSI 4100	60 min	ISO 16000-3
175	TSI 4100	15 min und 2 h	SS-ISO 16000:3
184	DryCal DC Lite	117 - 120 min	IFA 6045
230	TSI 4100	30 Minuten	DIN EN ISO 16000-3
236	Definer 220 Bios DryCal	2 h	interne SOP 81.40 angelehnt an NIOSH-Methode Nr. 2016
265	Gilian Gilibrator	10-40 min	DIN ISO 16000-3
285	DryCal Defender 310	zwischen 10 und 60 min mehrere Wiederholungen	DIN ISO 16000-3 (2013-01)
291	interne Geräteanzeige	120 min	DIN EN ISO 16000-3:2013-01

Proficiency testing scheme Aldehydes with sampling 2/2018

Participant	Volume flow measurement	Sampling time	Analytical method
508	Gilian Gilibrator	10-40 min	DIN ISO 16000-3

Participant	Date start sample preparation	Storage time after desorption	Date of analysis
2	22.10.2018	Ja, für 2 Tage im Kühlschrank bei 4°C.	24.10.2018
23	29.10.2018	nein	29.10.2018
33	18.10.2018	Im Kühlschrank < 1 Tage	18.10.2018
97	26.10.2018		26.10. - 27.10.2018
159	19.10.2018	6 Tage Raumtemperatur	25.10.2018 und 14.11.2018
171	22.10.2018	k.A.	23.10.2018
175	6. und 7. Nov	1 Tag	6. und 7. Nov
184	24.10.2018	Messung erfolgte direkt nach der Desorption	24.10.2018
230	22.10.2018	nein	22.10. 2018
236	18.10.2018	nein	18.10.2018
265	18.10.2018	1 Tag / -18°C	18.10.2018
285	19.10.2018	nein umgehende Analyse	19.10.2018
291	17.10.2018	ja, über Nacht, Kühlschrank	18.10.2018
508	18.10.2018	1 Tag/ -18°C	18.-19.10.2018

Participant	Desorption solution	Volume of desorption solution
2	Acetonitril und 85% Phosphorsäure	5 mL Acetonitril und 25µL Phosphorsäure
23	Acetonitril	5ml
33	Acetonitril	6 ml
97	Acetonitril	
159	Acetonitril mit DNPH u. H3PO4 (in 200 ml ACN: 250 mg DNPH)	5 ml
171	Acetonitril	1 ml
175	Acetonitril	2 ml
184	Acetonitril	5 ml
230	Acetonitril	10 ml
236	Acetonitril	3 ml
265	Acetonitril	2 ml

Proficiency testing scheme Aldehydes with sampling 2/2018

Participant	Desorption solution	Volume of desorption solution
285	Acetonitril	2 ml
291	Acetonitril	5 ml
508	Acetonitril	2 ml

Participant	Chromatography system	Autosampler
2	Agilent 1200 SL	Nein
23	HPLC/DAD 20A Shimadzu System	nein
33	BinPump G1312A HP, DAD G1315A HP, ALS G1313A HP	Nein, Raumtemperatur
97	HPLC-Anlage Shimadzu LC 10	
159	Tern. Gradientenpumpe, DAD (HP 1100/1200 Serie Agilent)	nein
171	Agilent Technologies 1260, DAD Detektor	nicht gekühlt
175	Vanquish Thermo	Ja 10
184	Agilent 1100 Serie	Ungekühlt
230	Fa. Agilent	nein
236	Agilent Technologies Infinity 1260 mit DAD Detektor	nein
265	Shimadzu	ja, 15°C
285	HPLC Dionex U-3000, Pumpe: LPG-3400 SD, Detektor: DAD-3000; Autosampler: WPS-3000SL	ungekühlt
291	API 2000 Gerät (LC-MS/MS), MS-Detektor, negativ Modus	ja, 20°C
508	Shimadzu	ja, 15°C

Participant	Analytical column	Flow rate HPLC
2	Ascentis Express RP-Amide	0,6mL/Min
23	Synergi 4µmHydro-RP 80A LC Column 250x4,6mm	1ml/min
33	Dr. Maisch Reprosil pur 120 C18-AQ 150x4 mm	1,2 ml/min
159	ODS Hypersil 250x4.0mm; 5µm von Agilent mit Vorsäule	0,8 ml/min
171	Nucleodur C18 (Isis 3µm, 250x4mm), Machery&Nagel	0.5 ml/min
175	Synchronis C18, 100x2,1 mm 1,7µ	0,3 ml/min
184	EC 50/3 NUCLEODUR Sphinx RP, 1,8im	0,9 ml/min
230	MZ PAH C 18, 5 µm	0,5ml/min
236	Pursuit C18 100x2,0 mm 3µm	0,2 ml/min

Proficiency testing scheme Aldehydes with sampling 2/2018

Participant	Analytical column	Flow rate HPLC
265	Agilent Zorbax RRHD Eclipse Plus C18, 2,1x150mm, 1,8µm	0,25 ml/min
285	Restek Allure AK 5µm, 200x4.6mm	1,5 ml/min
291	Phenomenex C18 Gemini 150 mm Länge; 3 mm ID; 5 fµm Partikelgröße	0,4 ml/min
508	Agilent Zorbax RRHD Eclipse Plus C18, 2,1x150mm, 1,8 µm	0,25 ml/min

Participant	Mobile phase
2	Wasser/Acetonitril
23	A: Wasser, B: Acetonitril+5% Wasser
33	Eluent A: Acetonitril Eluent B: Wasser
159	Methanol/Wasser/Acetonitril
171	Acetonitril/Wasser
175	Acetonitril/Wasser
184	H2O+10% THF / ACN
230	dest. Wasser/Acetonitril, Gradientenprogramm
236	Wasser/Acetonitril 40:60
265	Acetonitril/Wasser 55:45
285	Acetonitril / Wasser
291	A: 50 % ACN 50 % Wasser 100 mM Ammoniumacetat 0,04 % Ammoniumhydroxid; B:90 % ACN 10 % Wasser 100 mM Ammoniumacetat 0,04 % Ammoniumhydroxid
508	Acetonitril / Wasser 55:45

Participant	Recovery rate	Wavelength	Column temperature
2	Nein	360 nm bzw . 370 nm	30°C
23	nein	360nm	25° C
33	Nein, da Wiederfindung in Ordnung	365 nm	Raumtemperatur
159	ja	365 nm; 4 nm BW	27°C
171	nein	365.4; Ref 590	30°C
175	Nein	360	10
184	nein	360 nm	40°C
230	nein	362	40°C
236	nein	360 nm	33 Grad

Proficiency testing scheme Aldehydes with sampling 2/2018

Participant	Recovery rate	Wavelength	Column temperature
265	nein	356 nm	45°C
285	nein	360 nm	30°C
291	nein	s. o.	30°C Säulenofentemp.
508	nein	356 nm	45 °C
