Summary of laboratory means

Sample 1

	Formaldehyde	Z score	Acetaldehyde	Z score	Propionaldehyde	Z score
Unit	mg/m³		mg/m³		mg/m³	
–	–	– –	–	– –	–	– –
5	0,084	-0,91	0,528	-1,18	0,539	-1,56
34	0,112	2,16 E	0,721	2,05 E	0,821	2,85 E
40	0,088	-0,49	0,617	0,31	0,639	0,00
72	0,072	-2,19 E	0,474	-2,08 E	0,507	-2,07 E
107	0,090	-0,23	0,598	-0,01	0,604	-0,55
111	0,090	-0,23	0,600	0,02	0,610	-0,45
152	0,115	2,48 E	0,710	1,86	0,740	1,58
158	0,087	-0,56	0,590	-0,14	0,620	-0,30
159	0,097	0,53	0,644	0,76	0,773	2,10 E
191	0,087	-0,56	0,610	0,19	0,633	-0,09
197	0,132	4,33 FE	0,492	-1,78	0,543	-1,50
–	–	– –	–	– –	–	– –
Method	ISO 5725-2		ISO 5725-2		ISO 5725-2	
Assessment	|Z|<=2,00		|Z|<=2,00		|Z|<=2,00	
Mean	0,092		0,599		0,639	
Reproducibility s.d.	0,013		0,079		0,100	
Rel. reproducibility s.d.	14,00 %		13,14 %		15,67 %	
Reference value	0,082		0,572		0,612	
Target s.d.	0,009		0,060		0,064	
Rel. target s.d.	10,00 %		10,00 %		10,00 %	
Low er limit of tolerance	0,074		0,479		0,511	
Upper limit of tolerance	0,111		0,718		0,767	
Type B outliers	0		0		0	

	Formaldehyde	Z score	Acetaldehyde	Z score	Propionaldehyde	Z score
Type E outliers	4		2		3	
Type F outliers	1		0		0	
No. of laboratories after elimination of outliers type A-D and F (w ithout laboratories that only gave states but no measured values)	10		11		11	
Explanation of outlier types						
A: Single outlier						
B: Differing laboratory mean						
C: Excessive laboratory s.d.						
D: Excluded manually						
E: score outside tolerance limits						
F: |Score|>3,5						

Summary of laboratory means

Sample 2

	Formaldehyde	Z score	Propionaldehyde	Z score	Butyraldehyde	Z score
Unit	mg/m³		mg/m³		mg/m³	
–	–	– –	–	– –	–	– –
5	0,052	-0,98	0,857	-1,79	0,865	-1,77
34	0,068	1,82	1,246	1,93	1,196	1,38
40	0,053	-0,72	1,034	-0,10	1,034	-0,16
72	0,061	0,60	1,167	1,17	1,073	0,21
107	0,050	-1,31	0,882	-1,56	0,936	-1,09
111	0,060	0,43	1,060	0,15	1,070	0,19
152	0,071	2,34 E	1,240	1,87	1,180	1,23
158	0,052	-0,96	0,992	-0,50	1,288	2,26 E
159	0,057	-0,09	1,191	1,40	1,107	0,54
191	0,051	-1,14	0,979	-0,63	0,972	-0,75
197	0,089	5,47 BE	0,843	-1,93	0,835	-2,05 E
–	–	– –	–	– –	–	– –
Method	ISO 5725-2		ISO 5725-2		ISO 5725-2	
Assessment	|Z|<=2,00		|Z|<=2,00		|Z|<=2,00	
Mean	0,058		1,045		1,051	
Reproducibility s.d.	0,007		0,150		0,141	
Rel. reproducibility s.d.	12,80 %		14,35 %		13,43 %	
Reference value	0,050		0,916		0,922	
Target s.d.	0,006		0,104		0,105	
Rel. target s.d.	10,00 %		10,00 %		10,00 %	
Low er limit of tolerance	0,046		0,836		0,840	
Upper limit of tolerance	0,069		1,254		1,261	
Type B outliers	1		0		0	

	Formaldehyde	Z score	Propionaldehyde	Z score	Butyraldehyde	Z score
Type E outliers	2		0		2	
Type F outliers	0		0		0	
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	10		11		11	
Explanation of outlier types						
A: Single outlier						
B: Differing laboratory mean						
C: Excessive laboratory s.d.						
D: Excluded manually						
E: score outside tolerance limits						
F: |Score|>3,5						

Summary of laboratory means

Sample 3

	Formaldehyde	Z score	Acetaldehyde	Z score	Propionaldehyde	Z score	Butyraldehyde	Z score
Unit	mg/m³		mg/m³		mg/m³		mg/m³	
–	–	– –	–	– –	–	– –	–	– –
5	0,116	-1,42	0,423	-1,14	0,427	-1,47	0,432	-1,43
34	0,162	1,94	0,543	1,38	0,609	2,17 E	0,583	1,57
40	0,124	-0,86	0,488	0,22	0,503	0,05	0,505	0,02
72	0,130	-0,42	0,478	0,01	0,503	0,05	0,465	-0,78
107	0,123	-0,93	0,456	-0,45	0,449	-1,03	0,423	-1,61
111	0,140	0,32	0,500	0,47	0,490	-0,21	0,510	0,12
152	0,167	2,31 E	0,583	2,21 E	0,600	1,99	0,571	1,33
158	0,125	-0,79	0,472	-0,11	0,492	-0,17	0,643	2,76 E
159	0,126	-0,71	0,451	-0,55	0,523	0,45	0,506	0,04
191	0,123	-0,93	0,478	0,01	0,492	-0,17	0,491	-0,26
197	0,156	1,50	0,379	-2,06 E	0,418	-1,65	0,416	-1,75
–	–	– –	–	– –	–	– –	–	– –
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	0,136		0,477		0,501		0,504	
Reproducibility s.d.	0,018		0,055		0,061		0,072	
Rel. reproducibility s.d.	13,13 %		11,46 %		12,20 %		14,21 %	
Reference value	0,117		0,441		0,477		0,476	
Target s.d.	0,014		0,048		0,050		0,050	
Rel. target s.d.	10,00 %		10,00 %		10,00 %		10,00 %	
Low er limit of tolerance	0,109		0,382		0,400		0,403	
Upper limit of tolerance	0,163		0,573		0,601		0,605	
Type B outliers	0		0		0		0	

	Formaldehyde	Z score	Acetaldehyde	Z score	Propionaldehyde	Z score	Butyraldehyde	Z score
Type E outliers	1		2		1		1	
Type F outliers	0		0		0		0	
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	11		11		11		11	

Explanation of outlier types

A: Single outlier

B: Differing laboratory mean

C: Excessive laboratory s.d.

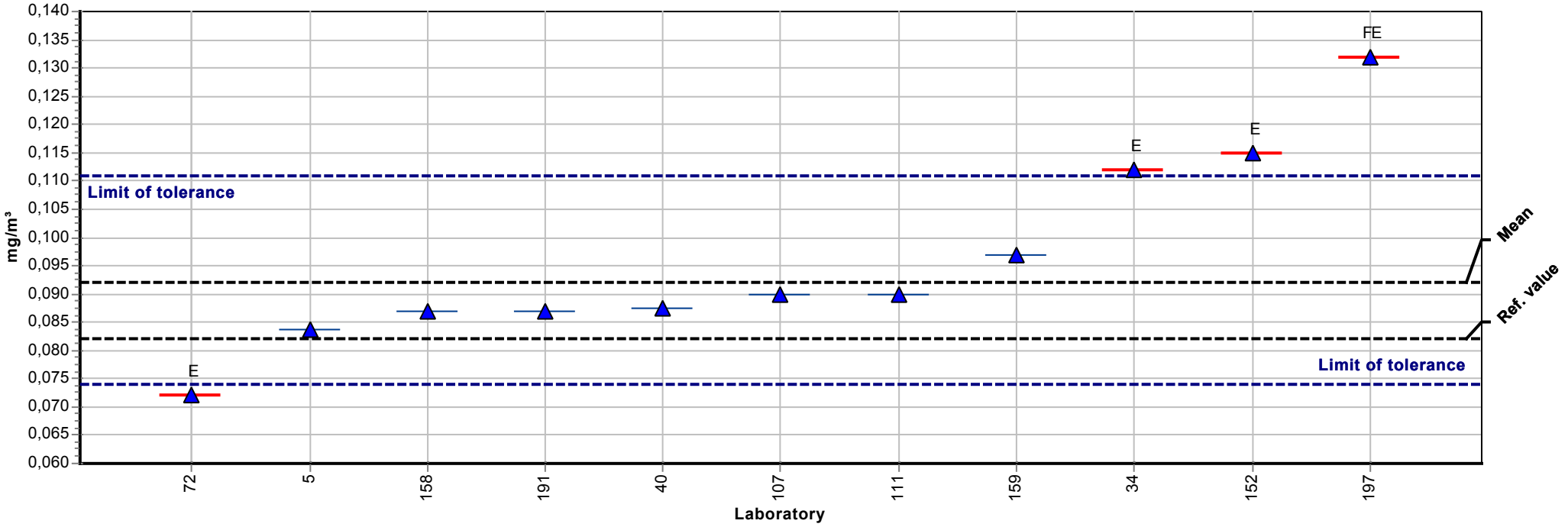
D: Excluded manually

E: score outside tolerance limits

F: |Score|>3,5

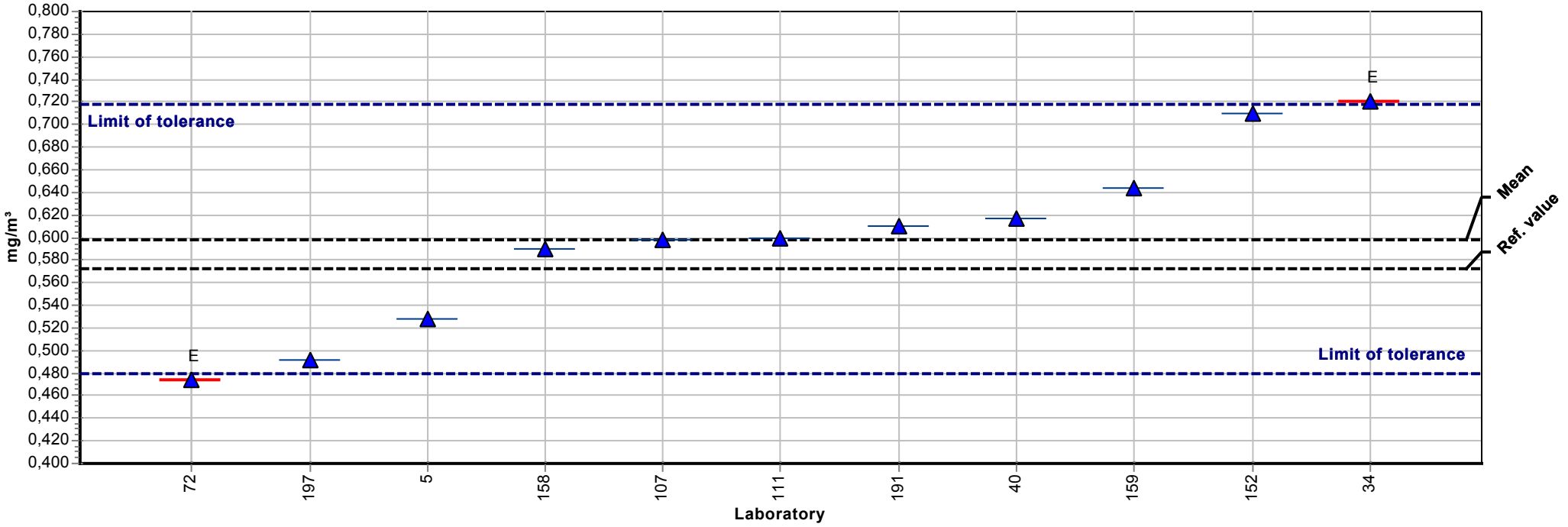
Summary results

Measurand:	**Formaldehyde**	**Mean:**	**0,092 mg/m³**
Sample:	**1**	**Reproducibility s.d.:**	**0,013 mg/m³**
Method:	**ISO 5725-2**	**Rel. reproducibility s.d.:**	**14,00%**
Rel. target s.d.:	**10,00% (Limited)**	**Reference value:**	**0,082 mg/m³**
No. of laboratories:	**10**	**Range of tolerance:**	**0,074 - 0,111 mg/m³ (|Z Score| <= 2,00)**



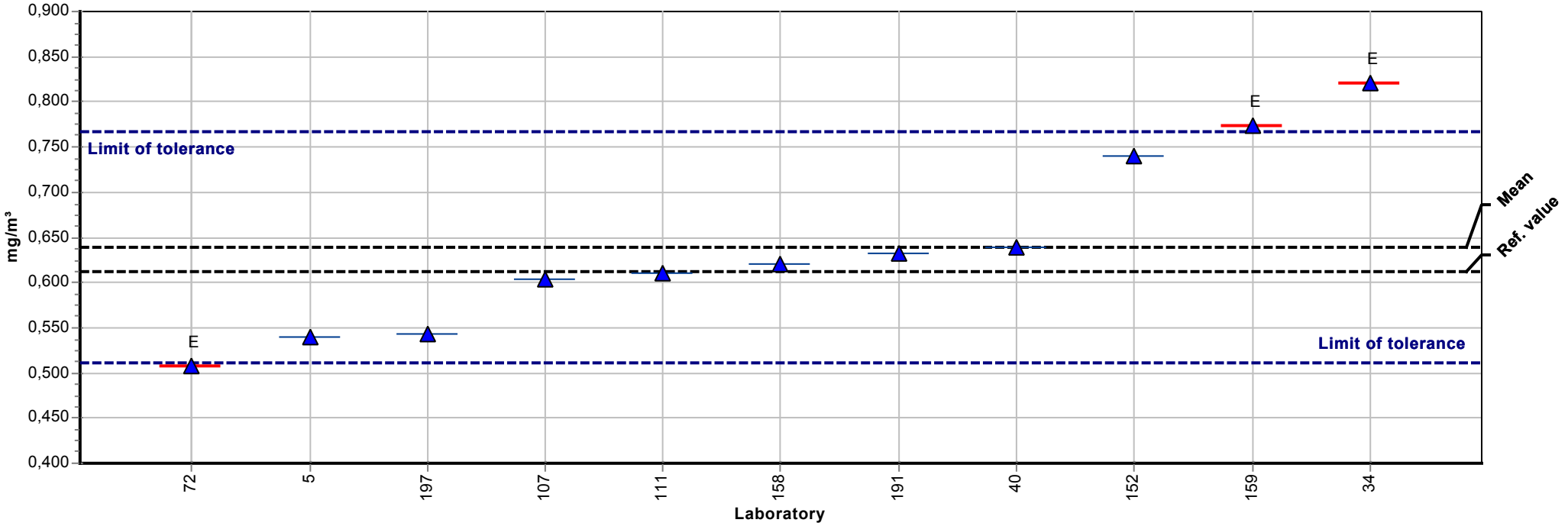
Summary results

Measurand:	**Acetaldehyde**	**Mean:**	**0,599 mg/m³**
Sample:	**1**	**Reproducibility s.d.:**	**0,079 mg/m³**
Method:	**ISO 5725-2**	**Rel. reproducibility s.d.:**	**13,14%**
Rel. target s.d.:	**10,00% (Limited)**	**Reference value:**	**0,572 mg/m³**
No. of laboratories:	**11**	**Range of tolerance:**	**0,479 - 0,718 mg/m³ (|Z Score| <= 2,00)**



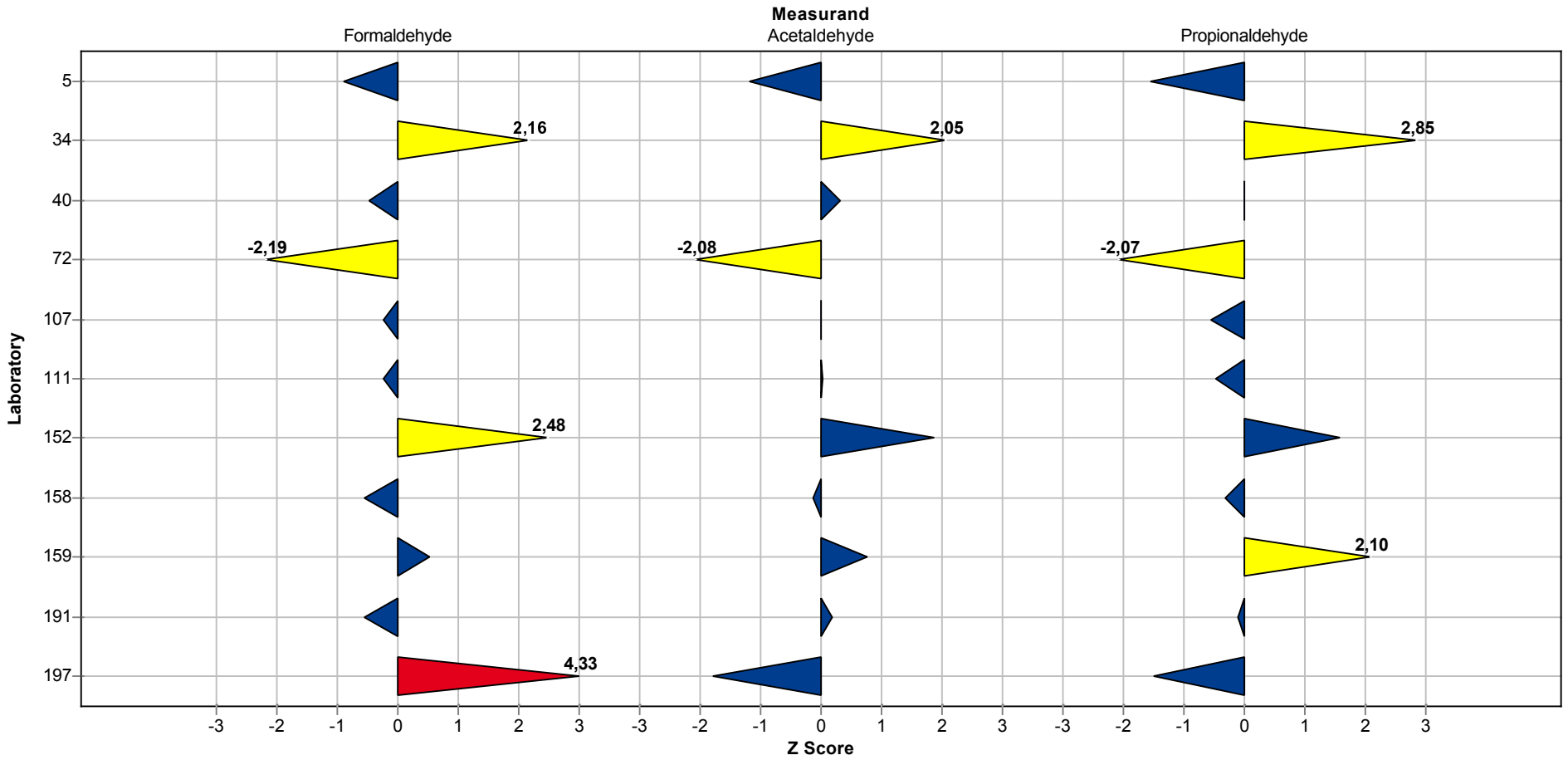
Summary results

Measurand:	Propionaldehyde	**Mean:**	0,639 mg/m³
Sample:	1	**Reproducibility s.d.:**	0,100 mg/m³
Method:	ISO 5725-2	**Rel. reproducibility s.d.:**	15,67%
Rel. target s.d.:	10,00% (Limited)	**Reference value:**	0,612 mg/m³
No. of laboratories:	11	**Range of tolerance:**	0,511 - 0,767 mg/m³ (|Z Score| <= 2,00)



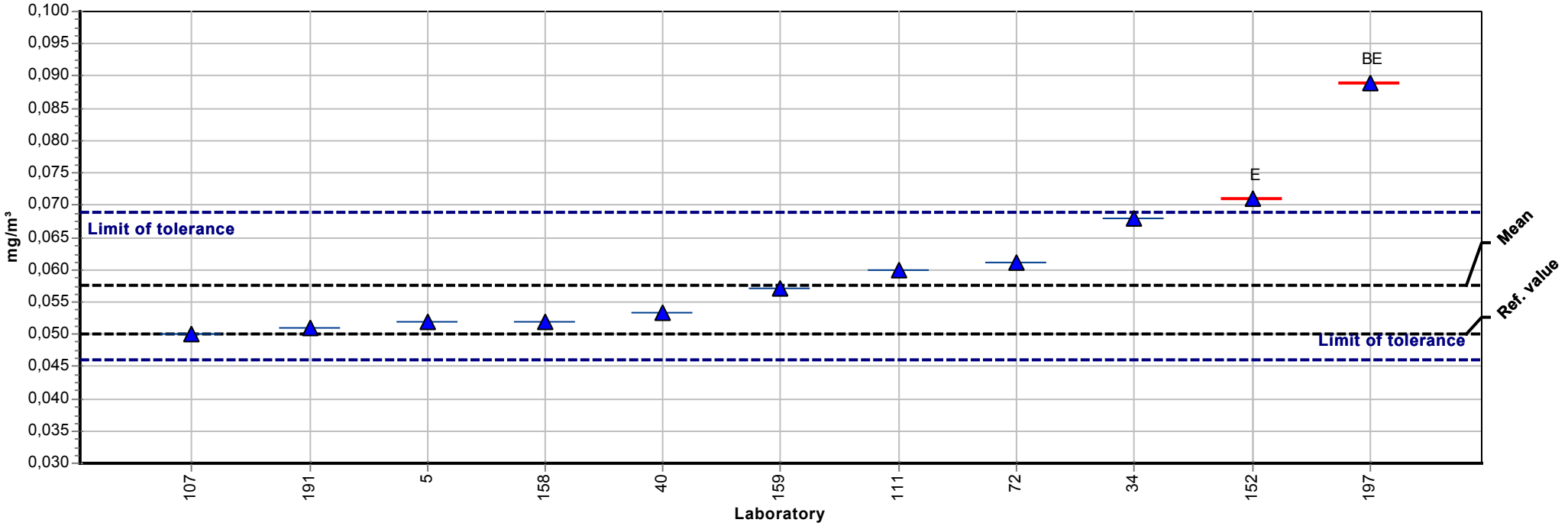
Sample chart of Z Scores

Sample 1



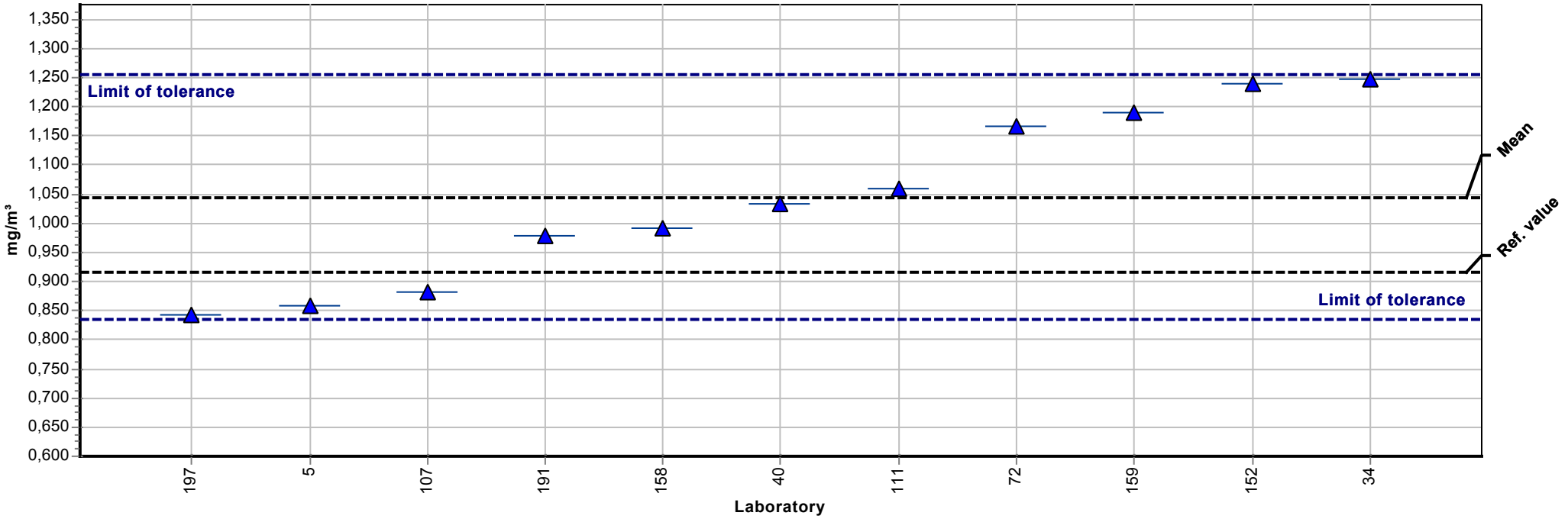
Summary results

Measurand:	**Formaldehyde**	**Mean:**	**0,058 mg/m³**
Sample:	**2**	**Reproducibility s.d.:**	**0,007 mg/m³**
Method:	**ISO 5725-2**	**Rel. reproducibility s.d.:**	**12,80%**
Rel. target s.d.:	**10,00% (Limited)**	**Reference value:**	**0,050 mg/m³**
No. of laboratories:	**10**	**Range of tolerance:**	**0,046 - 0,069 mg/m³ (|Z Score| <= 2,00)**



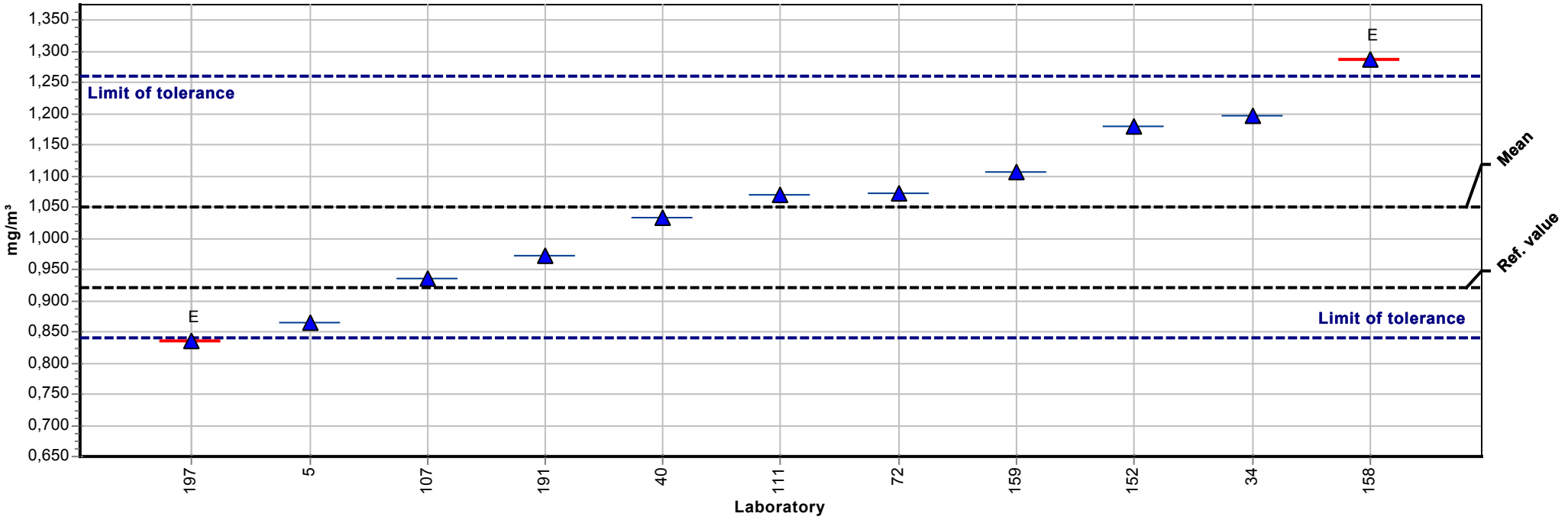
Summary results

Measurand:	Propionaldehyde	**Mean:**	1,045 mg/m³
Sample:	2	**Reproducibility s.d.:**	0,150 mg/m³
Method:	ISO 5725-2	**Rel. reproducibility s.d.:**	14,35%
Rel. target s.d.:	10,00% (Limited)	**Reference value:**	0,916 mg/m³
No. of laboratories:	11	**Range of tolerance:**	0,836 - 1,254 mg/m³ (|Z Score| <= 2,00)



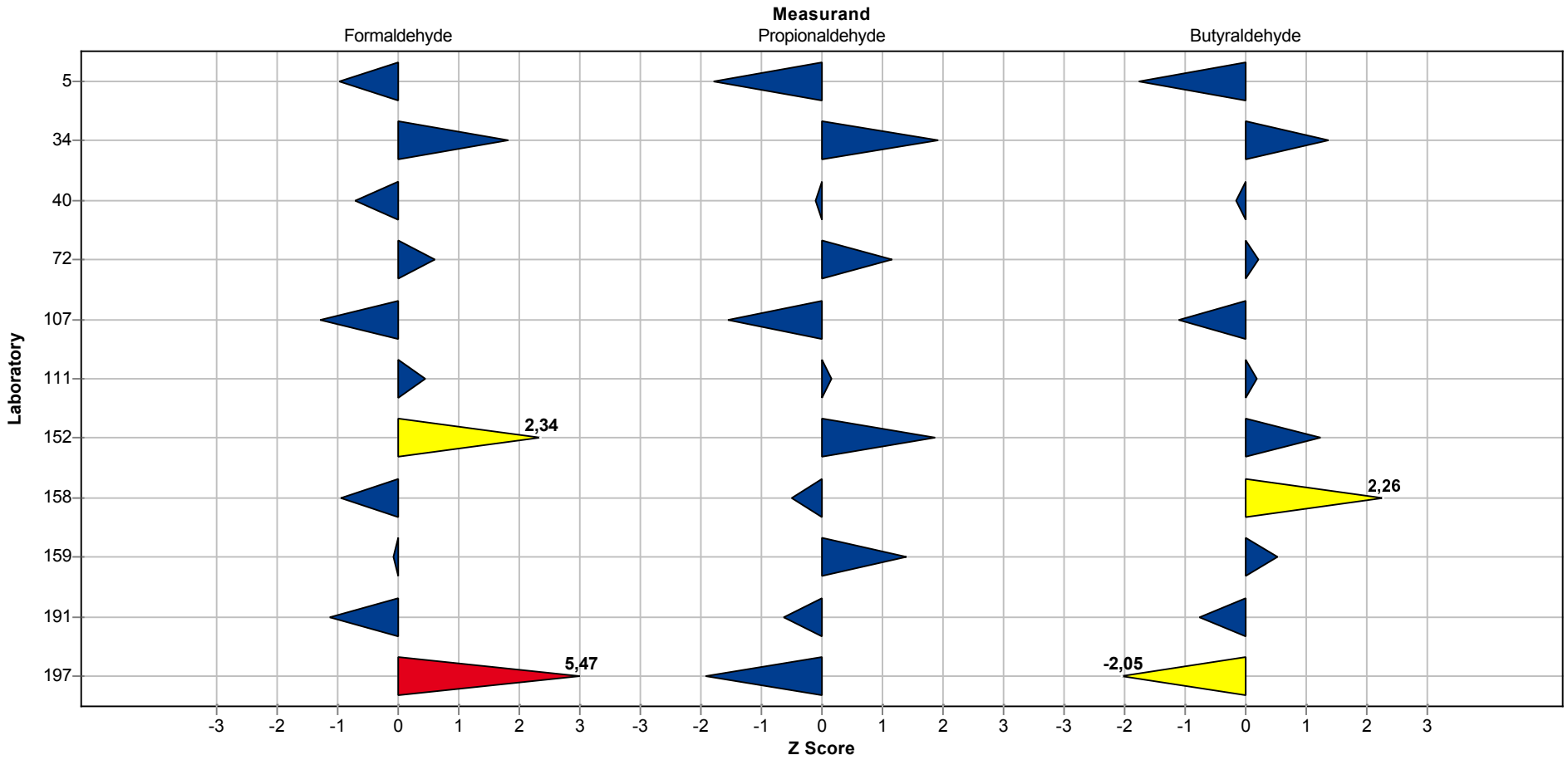
Summary results

Measurand:	**Butyraldehyde**	**Mean:**	**1,051 mg/m³**
Sample:	**2**	**Reproducibility s.d.:**	**0,141 mg/m³**
Method:	**ISO 5725-2**	**Rel. reproducibility s.d.:**	**13,43%**
Rel. target s.d.:	**10,00% (Limited)**	**Reference value:**	**0,922 mg/m³**
No. of laboratories:	**11**	**Range of tolerance:**	**0,840 - 1,261 mg/m³ (|Z Score| <= 2,00)**



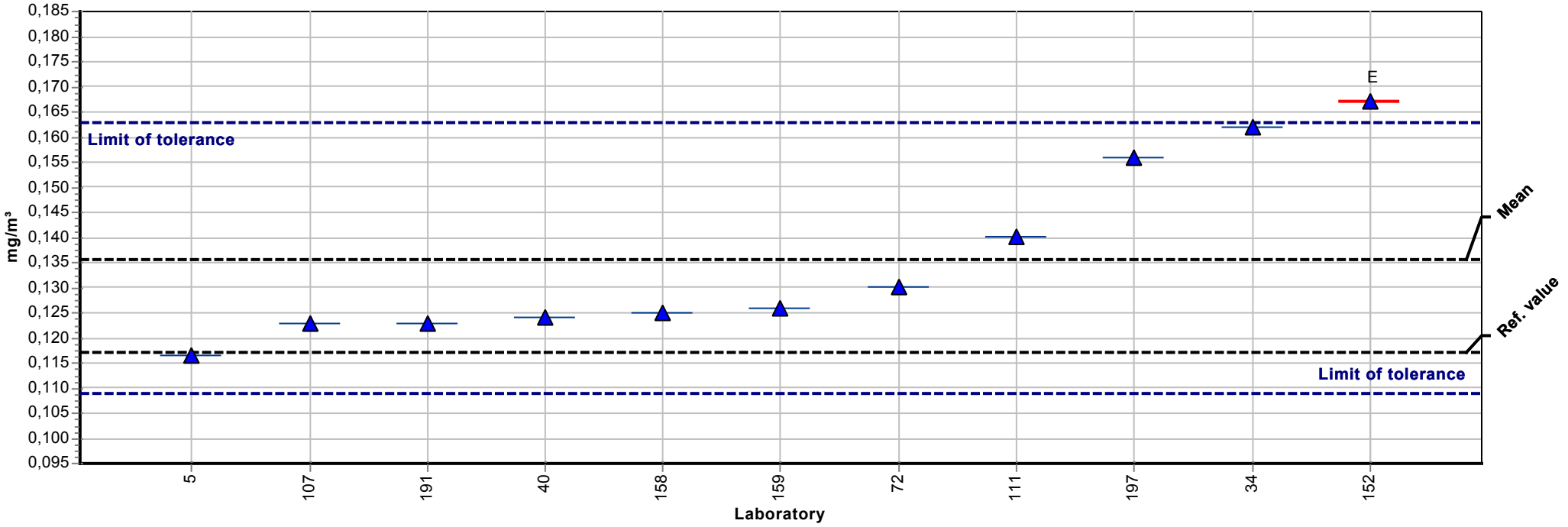
Sample chart of Z Scores

Sample 2



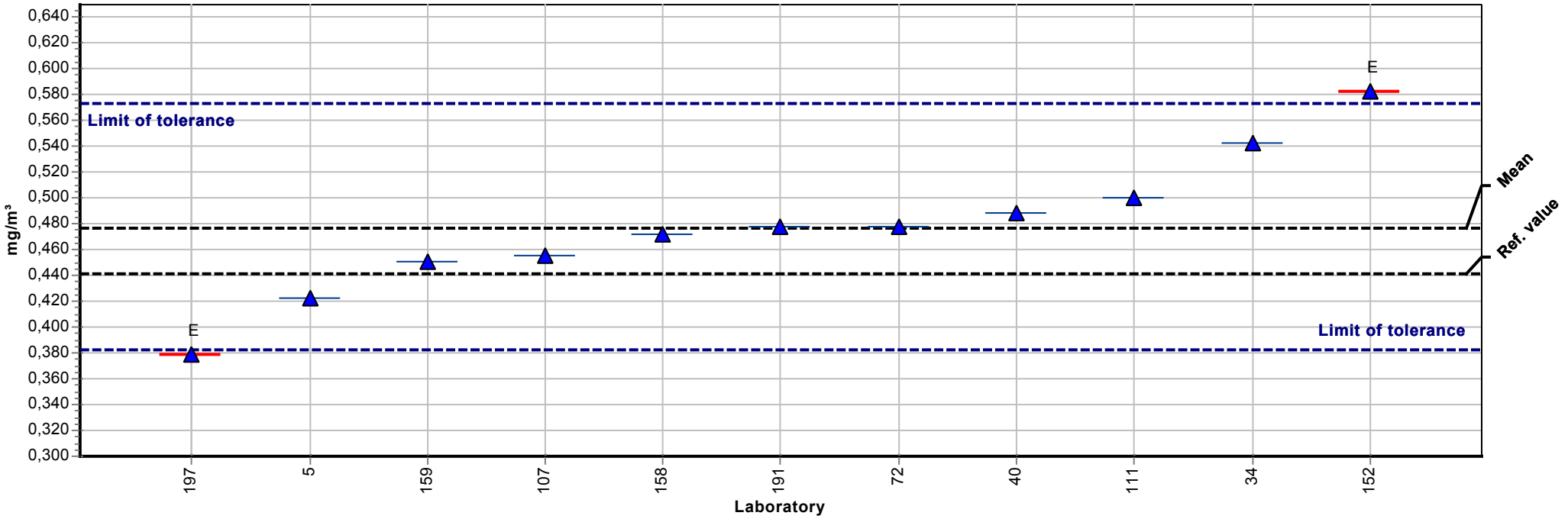
Summary results

Measurand:	**Formaldehyde**	**Mean:**	**0,136 mg/m³**
Sample:	**3**	**Reproducibility s.d.:**	**0,018 mg/m³**
Method:	**ISO 5725-2**	**Rel. reproducibility s.d.:**	**13,13%**
Rel. target s.d.:	**10,00% (Limited)**	**Reference value:**	**0,117 mg/m³**
No. of laboratories:	**11**	**Range of tolerance:**	**0,109 - 0,163 mg/m³ (|Z Score| <= 2,00)**



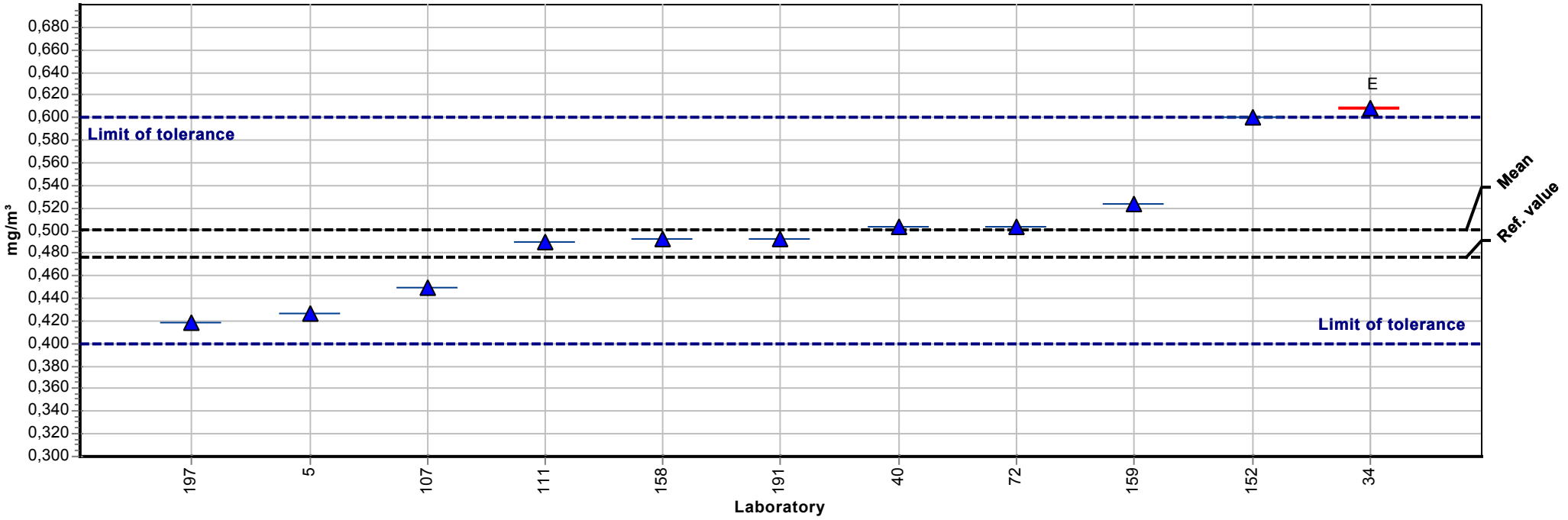
Summary results

Measurand:	**Acetaldehyde**	**Mean:**	**0,477 mg/m³**
Sample:	**3**	**Reproducibility s.d.:**	**0,055 mg/m³**
Method:	**ISO 5725-2**	**Rel. reproducibility s.d.:**	**11,46%**
Rel. target s.d.:	**10,00% (Limited)**	**Reference value:**	**0,441 mg/m³**
No. of laboratories:	**11**	**Range of tolerance:**	**0,382 - 0,573 mg/m³ (|Z Score| <= 2,00)**



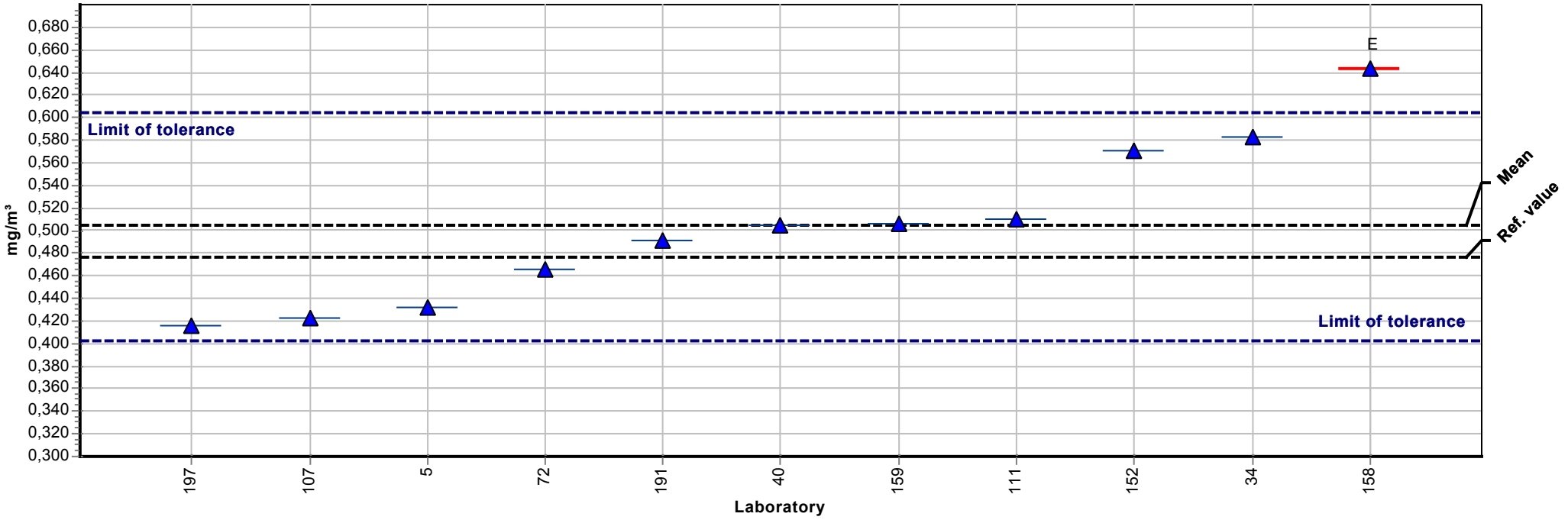
Summary results

Measurand:	Propionaldehyde	**Mean:**	0,501 mg/m³
Sample:	3	**Reproducibility s.d.:**	0,061 mg/m³
Method:	ISO 5725-2	**Rel. reproducibility s.d.:**	12,20%
Rel. target s.d.:	10,00% (Limited)	**Reference value:**	0,477 mg/m³
No. of laboratories:	11	**Range of tolerance:**	0,400 - 0,601 mg/m³ (|Z Score| <= 2,00)



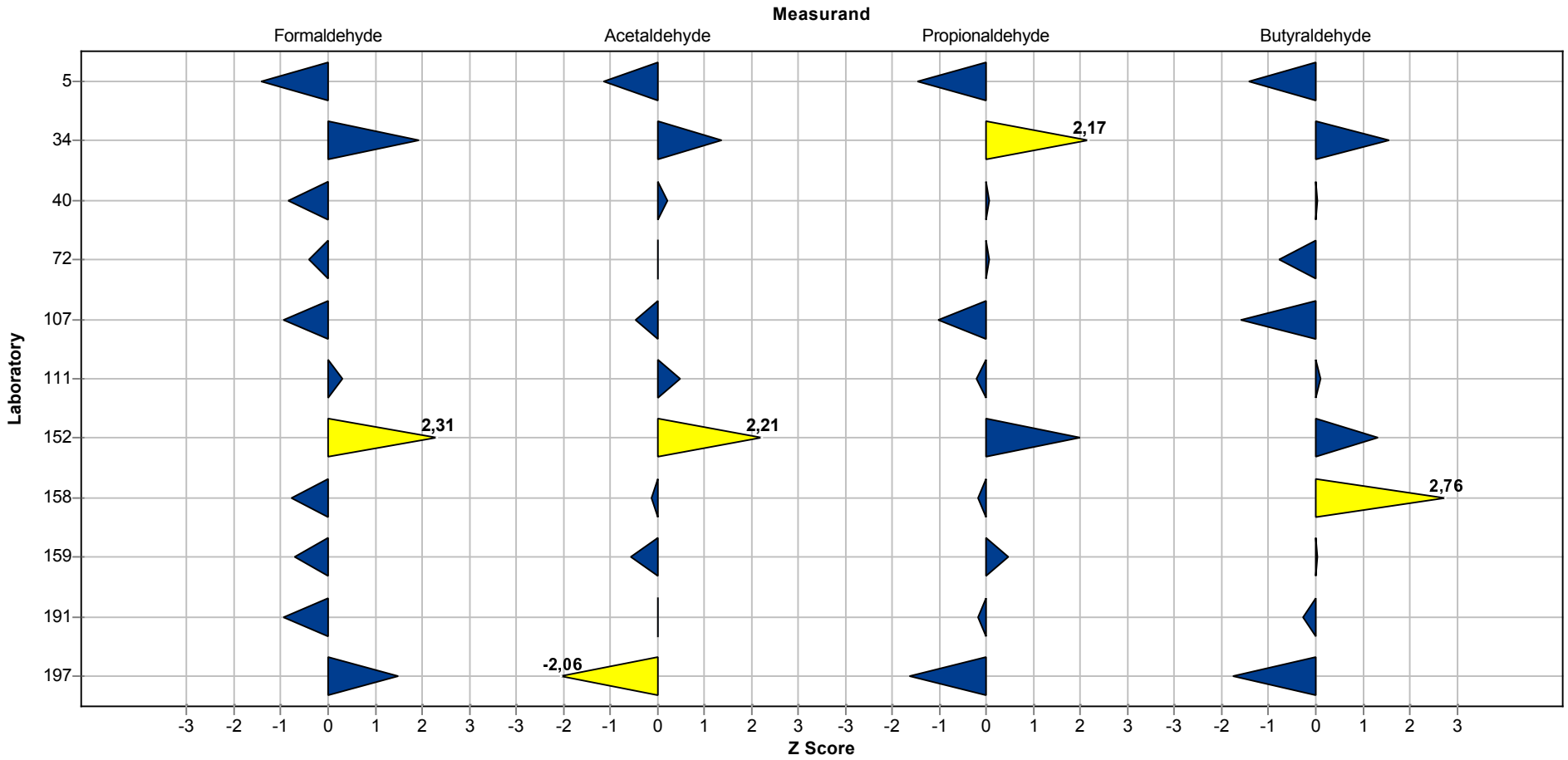
Summary results

Measurand:	Butyraldehyde	**Mean:**	0,504 mg/m³
Sample:	3	**Reproducibility s.d.:**	0,072 mg/m³
Method:	ISO 5725-2	**Rel. reproducibility s.d.:**	14,21%
Rel. target s.d.:	10,00% (Limited)	**Reference value:**	0,476 mg/m³
No. of laboratories:	11	**Range of tolerance:**	0,403 - 0,605 mg/m³ (|Z Score| <= 2,00)



Sample chart of Z Scores

Sample 3



Questions and Answers

Participant	kind of tube	kind of pump	volume flow
34	LP DNPH SUPELCO	SG350	0,33 l/min
40	Waters Sep-Pak Plus-Short Body (360mg)	Gilian LFS 113	200 ml/min
72	DNPH Kartuschen XPoSure Aldeyde Sampler, Fa. Waters	Gil Air und SG 350	333 ml/min
107	LpDNH H10 Kartuschen von Supelco	GSA SG4000 / Gilian	0,3l/min / 0,5l/min
111	DNPH-Kartusche	GSA SG 4000	0,5 bis 1,0 l/min
152	DNPH Supelco	Turzer	1.5 Liter/min
158	Supelco LpDNPH S10	GSA SG 4000 und Gillan PP5 - Ex	0,5 L/min
159	Waters Sep-Pak, XPoSure Aldehyde, DNPH-Kartusche	GSA 4000ex, Gilian PP5-ex	1,0 Liter / min
191	WPOSURE DNPH CART. WATERS	Pompe Gilair LFS	330 ml/min
197	DNPN-Silicagel (SKC)	Firma GSA Typ SG4000ex	ca 0,5l

Participant	sampling time
34	2 h
40	Prüfgas 1 = 102 Minuten, Prüfgas 2 = 110 Minuten, Prüfgas 3 = 93 Minuten
72	60 min
107	120 min / 60 min
111	25 min bis 60 min
152	30 Minuten
158	30 min und 60 min
159	60 min
191	2 hours
197	120 min

Participant	method
34	HPLC Hausmethode
40	
72	Validierte Hausmethode AA.EZM/I.09
107	Hausmethode in Anlehnung IFA Methode 6045

Participant	method
111	VDI 3862 Bl. 3
152	DNPH
158	Bestimmung als Derivate von 2,4- Dinitrophenylhydrazin (2,4-DNPH) mittels Hochleistungs-Flüssigkeits-Chromatografie (HPLC) und UV-Absorption
159	SOP BGN 5P, HPLC, PN mit DNPH
191	ISO 16000-3 / ana 033 (internal method)
197	BGIA 7520

Participant	date start sample preparation	solvent
34	20.09.2012	Acetonitril
40	17.09.2012	Acetonitril
72	13.09.12	Acetonitril
107	19. Sept.	Acetonitril
111	17.09.2012	Acetonitril
152		
158	13.09.2012	LpDNPH S10 2,4- Dinitrophenylhydrazin
159	14.09.2012	Acetonitril mit DNPH u. H3PO4 (in 200ml AcN: 250mg DNPH + 2ml H3PO4)
191	13/09/12	acetonitrile
197	14.9.2012	Acetonitril

Participant	volume of desorption solution
34	2 ml
40	2 ml (Die Kartuschen w erden aufgeschnitten, der Kartuscheninhalt in ein Vial überführt und mit 2 ml überschichtet, dann 15 Minuten Ultraschallbad und Filtration in ein 1 ml - Vial)
72	2,7 ml
107	5 ml
111	5 ml
152	
158	2 x 2 ml und auf 5 aufgefüllt
159	5 ml
191	5 ml
197	5 ml

Participant	storage time after desorption
34	nein
40	keine - Direkte Messung nach der 15 minütigen Desorption im Ultraschallbad, allerdings Wartezeit nach abtrennen vom Adsorbens auf dem Autosampler bis zur Messung. Bei den jew eils 8 aufeinanderfolgenden Proben eines Prüfgases w urden durch die Wartezeit keine unterschiedlichen Konzentrationen erreicht Stabw n < = 1,2 %
72	15 min
107	1 - 7 Tage
111	<24 h
152	
158	1 Tag bei Raumtemperatur gelagert
159	48 h
191	no
197	30 min

Participant	date of analysis	Pumpe/Vordruck
34	20.9.2012	
40	17.09.2012 und 18.09.2012 bedingt durch Wartezeit auf Autosampler vor der Injektion	
72	13.09.12 - 18.09.12	Alliance 2695, Fa. Waters
107	20. - 27. Sept.	70 bar
111	17. und 26.09.2012, 04.10.2012	80 bar
152	21.9.2012	Agilent 1200 Series binäre Pumpe
158	14.09.2012	
159	17.09.2012 + 21.09.2012	Tern. Gradientenpumpe / Säulenabhängig
191	14/09/12	pump gradient/1700psi
197	24.9.2012	

Participant	injection volume	mobile phase
34	10 µl	Acetonitril /Methanol /Wasser 6:1:3
40	10 µl	Acetonitril / Wasser Am Anfang der Analyse 40 % Acetonitril - Gradient - bei 15 Minuten 80 % Acetonitril
72	10 µl	ACN- Wasser- THF
107	20 µl	ACN/H2O
111	10 µl	ACN/H2O 65/35
152		
158	5µL	Acetonitril/Wasser

Participant	injection volume	mobile phase
159	10 µl	Methanol / Wasser / Acetonitril
191	20 µl	w ater/THF/MeCN
197	20	ACN/Wasser 20:80

Participant	gradient/temperature program	flow rate
34	ohne	0.7 ml/min
40	40 °C	1,0 ml/min
72	5 min:35% ACN,55% Wasser,10%THF; nach 11 min: 50% ACN,50% Wasser; nach 21 min 100% ACN; Säulentemp. 30 Grad C	0,5 ml/min
107	Gradient 50%ACN - 100% ACN	0,6/min
111	isokratisch, 20 °C	0,8 ml/min
152		
158	Von 60% Acetonitril bis 100% Acetonitril in 30 min	1,000 ml/min
159	0-8,99 min: M52%/W31%/A17%; 9-28 min: M52%/W15%/A33%; 28+3 min: M52%/W31%/A17%	0,8 ml/min
191	60/10/30 --> 40/0/60 (22min) --> 20/0/80 (25min) --> 10/0/90 (30min)	1,2 ml/min
197	konstant über die angegebenen Peaks	1 ml

Participant	detector	avelength	analytical column/dimension
34	DAD	365 nm	ODS Hypersil 5µm 250x4.6 mm
40	DAD Detektor	363	LiChrospher 100 RP 18 endcapped 150 mm * 4 mm / 5 µm
72	PDA	210-500 nm, extracted channel 365 nm	Polaris 3, C18-A, S 150x3,0 mm Säule Fa. Varian
107	DAD	365 nm	Supelco LC18; 25cm x 4,6 cm x 5µm // Reprospher C-18 Aqua 5µm
111	UV-DAD	365 nm	C12, Phenominex, Max RP808 250 mmx4,6µ
152			
158	DAD-UV	360nm	Hypersil ODS 4.0 x 250mm 5 Micron
159	DAD (HP 1100/1200 Serie)	365 nm; 4nm Bw	ODS-Hypersil 250x4mm; 5µm von HP mit Vorsäule
191	UV (w aters 2487)	360 nm	reversed phase C18 5µm ; 3,9 x 150mm
197	DAD	365 nm	C-18 (5 µm)

Participant	recovery rate
34	ohne
40	100 %

Participant	recovery rate
72	-
107	87 - 93%
111	
152	
158	Es w urde ein unabhängiger Kontrollstandard verw endet
159	99 - 100%
191	
197	84-90%