

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

Proficiency testing scheme “Inorganic Acids”

- **Volatile inorganic acids: hydrochloric acid, HCl and nitric acid, HNO₃**
- **Non-volatile inorganic acids: phosphoric acid, H₃PO₄ and sulphuric acid, H₂SO₄**

March 2020

Summary of laboratory test results

Measurand hydrochloric acid

	Sample 1	Z score	Outlier type	Sample 2	Z score	Outlier type	Sample 3	Z score	Outlier type
Unit	mg/m ³			mg/m ³			mg/m ³		
26	3.800	0.73		0.760	0.61		4.300	0.44	
68	3.370	-0.48		0.516	-2.79	E	3.124	-2.41	E
78	3.524	-0.05		0.732	0.22		4.125	0.02	
83	3.409	-0.37		0.694	-0.30		3.945	-0.42	
135	3.420	-0.34		0.788	1.01		4.210	0.23	
138	3.400	-0.40		0.690	-0.36		3.710	-0.99	
177	4.660	3.16	BE	0.510	-2.88	E	2.370	-4.24	FE
178	5.370	5.16	BE	0.891	2.44	E	4.790	1.63	
197	3.720	0.50		0.800	1.17		4.430	0.76	
208	3.690	0.42		0.779	0.88		4.420	0.74	
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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	10			10			10		
Mean	3.542			0.716			4.117		
Reproducibility s.d.	0.170			0.121			0.483		
Rel. reproducibility s.d.	4.80 %			16.95 %			11.73 %		
Reference value	3.560			0.750			4.320		
Target s.d.	0.354			0.072			0.412		
Rel. target s.d.	10.00 %			10.00 %			10.00 %		
Lower limit of tolerance	2.833			0.573			3.294		
Upper limit of tolerance	4.250			0.859			4.940		
Type B outliers	2								
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)	8			10			9		

	Sample 1	Z score	Outlier type	Sample 2	Z score	Outlier type	Sample 3	Z score	Outlier type
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 of laboratory test results

Measurand nitric acid

	Sample 1	Z score	Outlier type	Sample 2	Z score	Outlier type	Sample 3	Z score	Outlier type
Unit	mg/m ³			mg/m ³			mg/m ³		
26	2.600	0.88		1.100	0.34		2.200	0.56	
68	2.298	-0.38		0.824	-2.25	E	1.707	-1.81	
78	2.284	-0.44		1.037	-0.25		2.063	-0.10	
83	2.242	-0.62		0.996	-0.64		1.994	-0.43	
135	2.320	-0.29		1.150	0.81		2.260	0.85	
138	2.400	0.04		1.080	0.15		2.300	1.04	
177	2.920	2.22	BE	1.210	1.38		1.950	-0.64	
178	2.450	0.25		1.010	-0.50		1.880	-0.98	
197	2.490	0.42		1.130	0.62		2.280	0.94	
208	2.420	0.13		1.100	0.34		2.200	0.56	
–	–	--		–	--		–	--	
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	10			10			10		
Mean	2.389			1.064			2.083		
Reproducibility s.d.	0.115			0.106			0.198		
Rel. reproducibility s.d.	4.80 %			10.00 %			9.51 %		
Reference value	2.340			1.110			2.440		
Target s.d.	0.239			0.106			0.208		
Rel. target s.d.	10.00 %			10.00 %			10.00 %		
Lower limit of tolerance	1.911			0.851			1.667		
Upper limit of tolerance	2.867			1.276			2.500		
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)	9			10			10		

	Sample 1	Z score	Outlier type	Sample 2	Z score	Outlier type	Sample 3	Z score	Outlier type
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 of laboratory test results

Measurand phosphoric acid

	Sample 1	Z score	Outlier type	Sample 2	Z score	Outlier type	Sample 3	Z score	Outlier type
Unit	mg/m ³			mg/m ³			mg/m ³		
26	0.690	0.42		0.360	0.60		0.880	0.29	
68	0.685	0.34		0.361	0.63		0.838	-0.20	
78	0.672	0.14		0.345	0.16		0.858	0.03	
83	0.596	-1.00		0.334	-0.18		0.836	-0.23	
135	0.655	-0.11		0.340	0.01		0.855	-0.01	
138	0.750	1.32		0.370	0.89		0.940	0.99	
177	0.660	-0.04		0.290	-1.46		0.890	0.40	
178	0.626	-0.55		0.314	-0.76		0.812	-0.51	
197	0.641	-0.32		0.340	0.01		0.826	-0.34	
208	0.649	-0.20		0.343	0.10		0.820	-0.41	
–	–	--		–	--		–	--	
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	10			10			10		
Mean	0.662			0.340			0.855		
Reproducibility s.d.	0.041			0.024			0.039		
Rel. reproducibility s.d.	6.26 %			6.93 %			4.55 %		
Reference value	0.668			0.346			0.860		
Target s.d.	0.066			0.034			0.086		
Rel. target s.d.	10.00 %			10.00 %			10.00 %		
Lower limit of tolerance	0.530			0.272			0.684		
Upper limit of tolerance	0.795			0.408			1.027		
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values)	10			10			10		
Explanation of outlier types									

	Sample 1	Z score	Outlier type	Sample 2	Z score	Outlier type	Sample 3	Z score	Outlier type
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

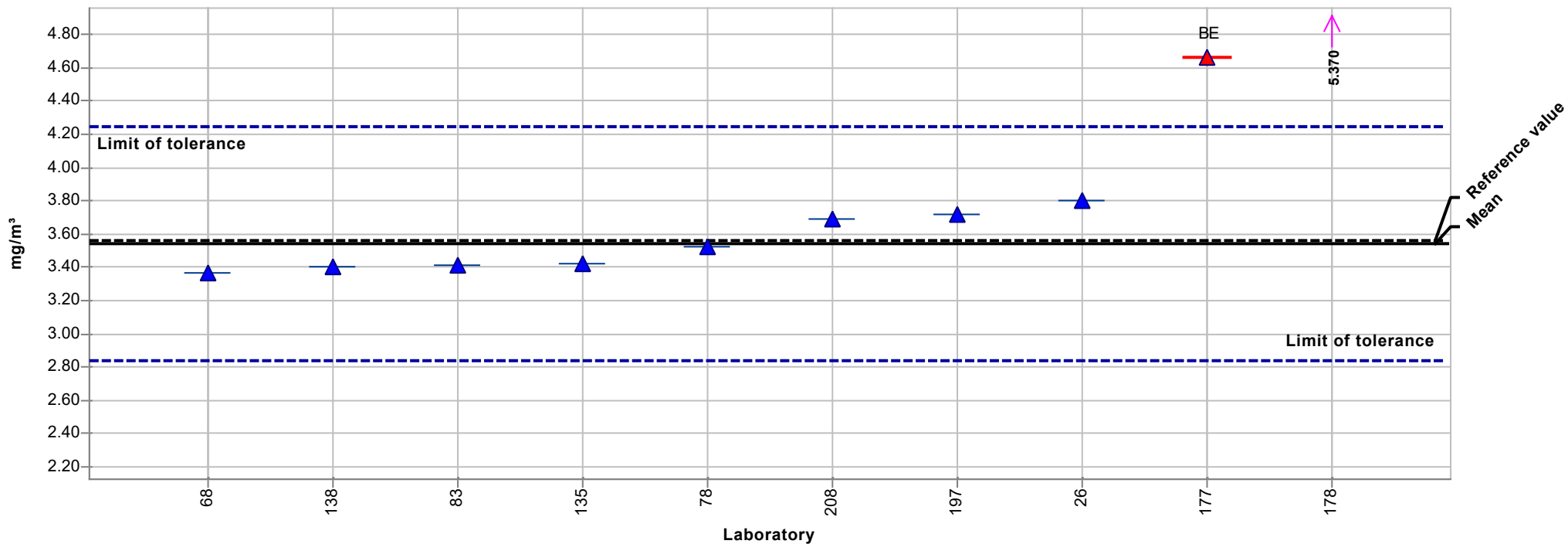
Measurand sulphuric acid

	Sample 1	Z score	Outlier type	Sample 2	Z score	Outlier type	Sample 3	Z score	Outlier type
Unit	mg/m ³			mg/m ³			mg/m ³		
26	0.0920	0.72		0.1700	0.33		0.0320	0.79	
68	0.0870	0.14		0.2230	3.55	FE	0.0650	11.91	BE
72	0.0810	-0.56		0.0960	-4.16	FE	0.0360	2.13	E
78	0.0879	0.24		0.1740	0.58		0.0272	-0.83	
83	0.0746	-1.31		0.1567	-0.48		0.0152	-4.88	BE
135	0.0920	0.72		0.1760	0.70		0.0300	0.11	
138	0.0880	0.25		0.1700	0.33		0.0290	-0.22	
177	0.0900	0.49		0.1600	-0.27		0.0300	0.11	
178	0.0760	-1.14		0.1480	-1.00		0.0240	-1.91	
197	0.0890	0.37		0.1720	0.45		0.0310	0.45	
208	0.0865	0.08		0.1540	-0.64		0.0278	-0.63	
-	-	--		-	--		-	--	
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	11			11			11		
Mean	0.0858			0.1645			0.0297		
Reproducibility s.d.	0.0060			0.0100			0.0033		
Rel. reproducibility s.d.	7.00 %			6.09 %			11.29 %		
Reference value	0.0930			0.1680			0.0310		
Target s.d.	0.0086			0.0165			0.0030		
Rel. target s.d.	10.00 %			10.00 %			10.00 %		
Lower limit of tolerance	0.0687			0.1316			0.0237		
Upper limit of tolerance	0.1030			0.1974			0.0356		
Type B outliers							2		
Type F outliers				2					
No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no	11			9			9		

	Sample 1	Z score	Outlier type	Sample 2	Z score	Outlier type	Sample 3	Z score	Outlier type
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									

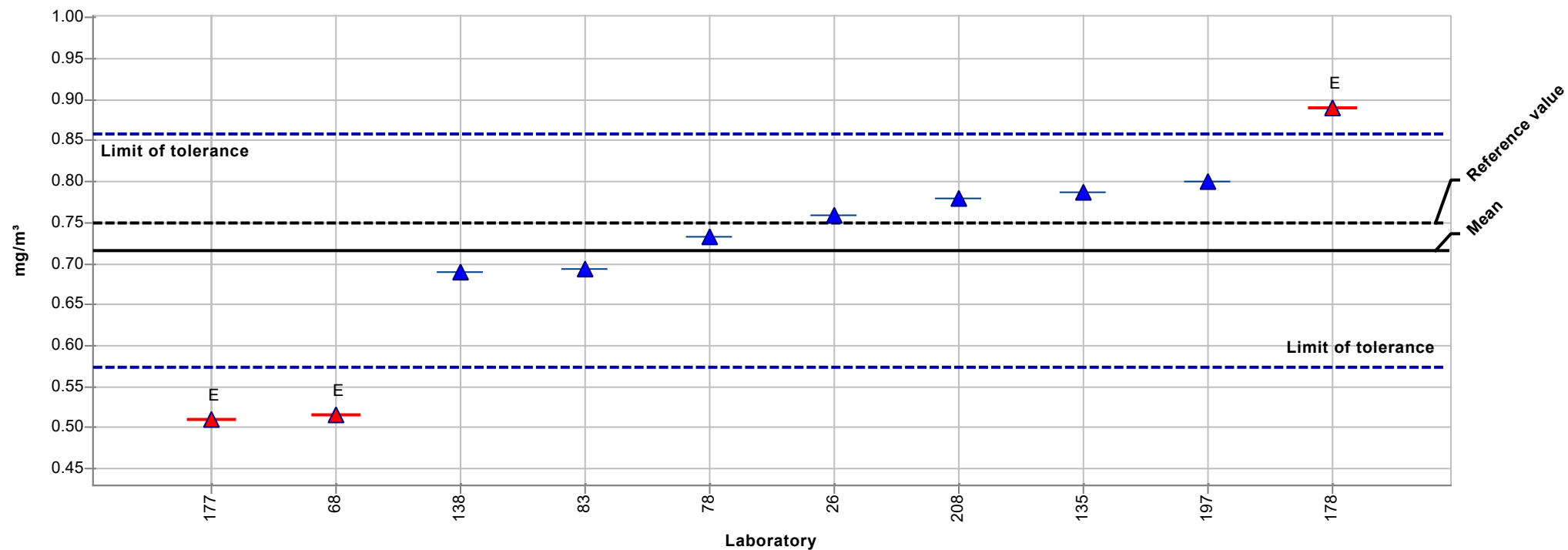
Summary results

Sample:	1	Mean:	3.542 mg/m ³
Measurand:	hydrochloric acid	Reproducibility s.d.:	0.170 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	4.80%
Rel. target s.d.:	10.00%	Reference value:	3.560 mg/m ³
Number of laboratories in calculation + outliers:	10	Range of tolerance:	2.833 - 4.250 mg/m ³ (Z-Score <= 2.00)



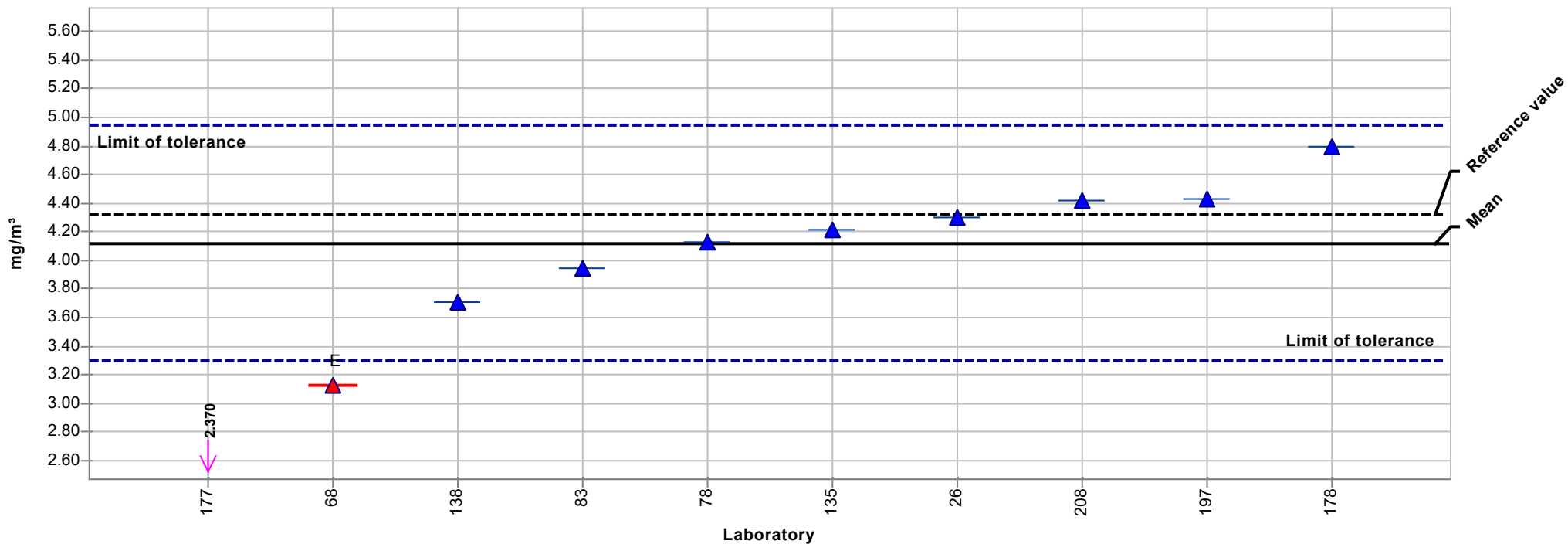
Summary results

Sample:	2	Mean:	0.716 mg/m ³
Measurand:	hydrochloric acid	Reproducibility s.d.:	0.121 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	16.95%
Rel. target s.d.:	10.00%	Reference value:	0.750 mg/m ³
Number of laboratories in calculation:	10	Range of tolerance:	0.573 - 0.859 mg/m ³ (Z-Score ≤ 2.00)



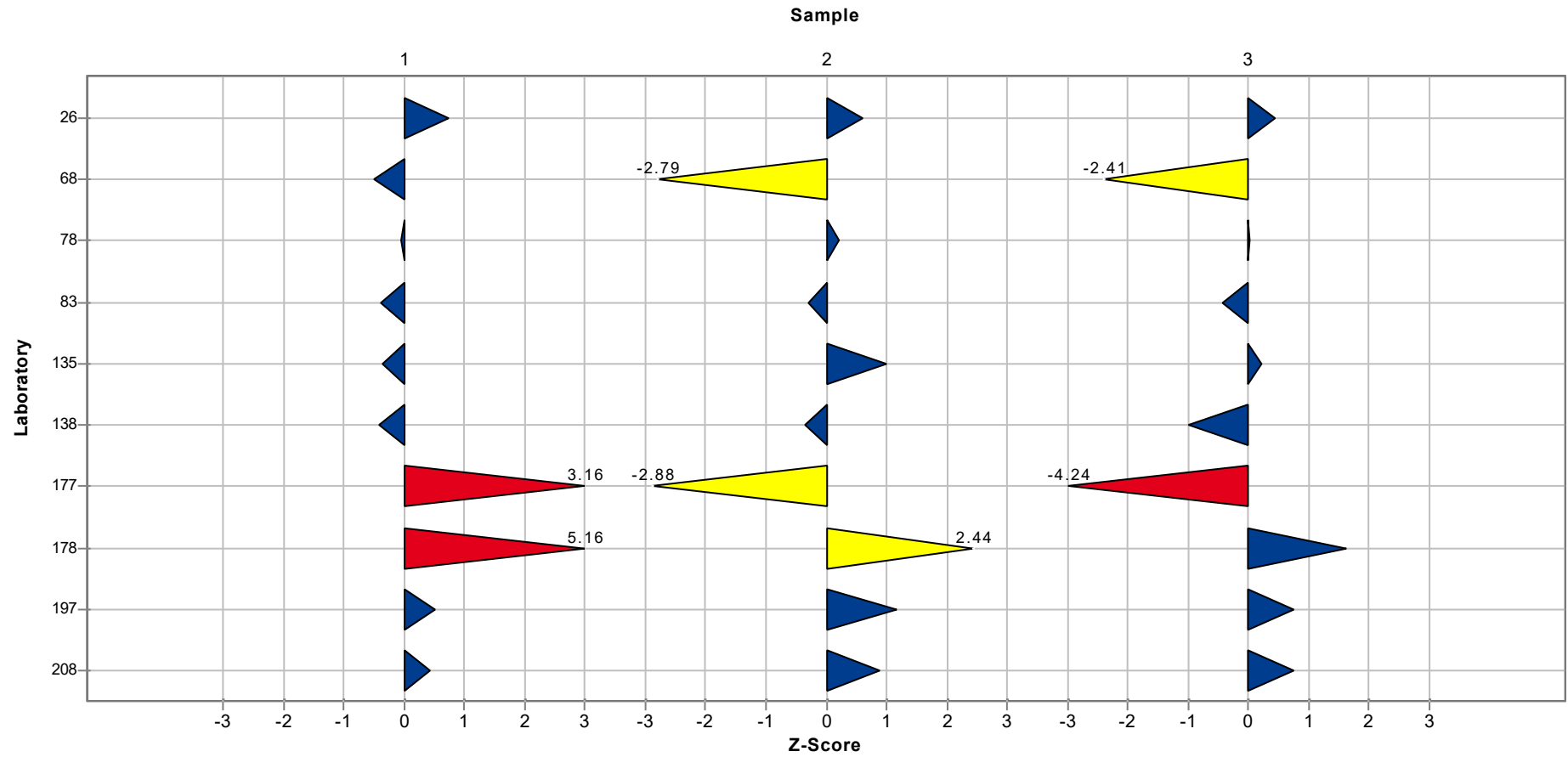
Summary results

Sample:	3	Mean:	4.117 mg/m ³
Measurand:	hydrochloric acid	Reproducibility s.d.:	0.483 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	11.73%
Rel. target s.d.:	10.00%	Reference value:	4.320 mg/m ³
Number of laboratories in calculation:	9	Range of tolerance:	3.294 - 4.940 mg/m ³ (Z-Score <= 2.00)



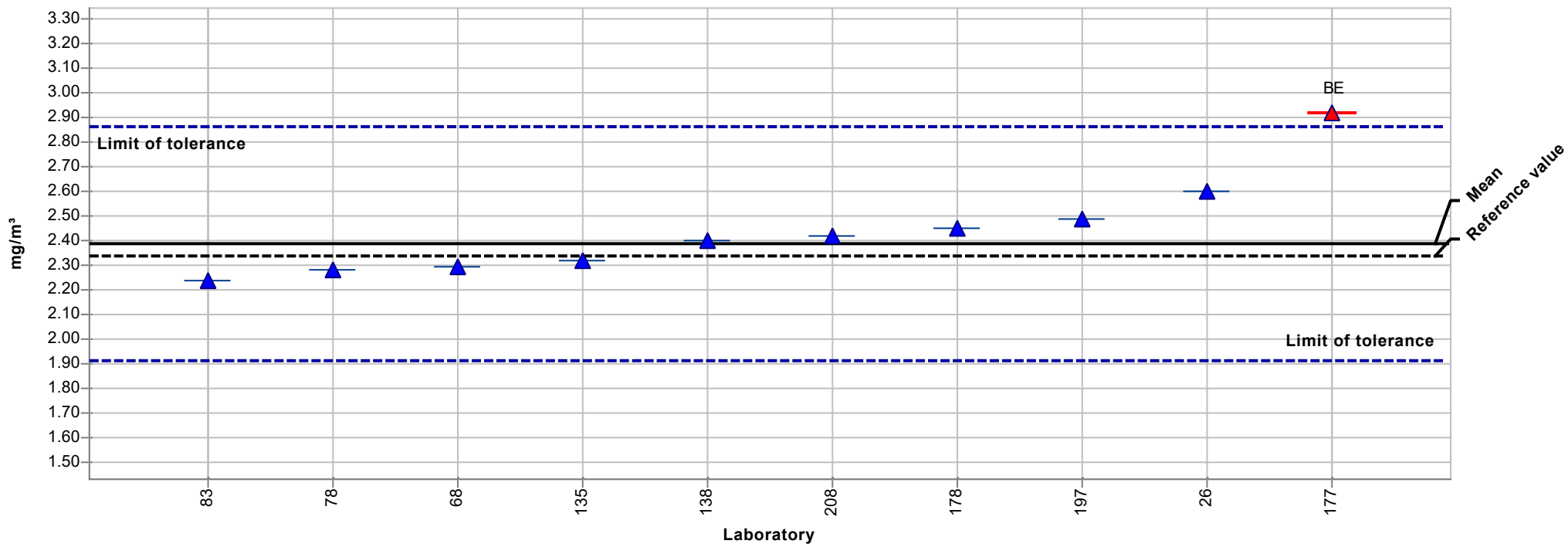
Analyte chart of Z-Scores

Measurand: hydrochloric acid



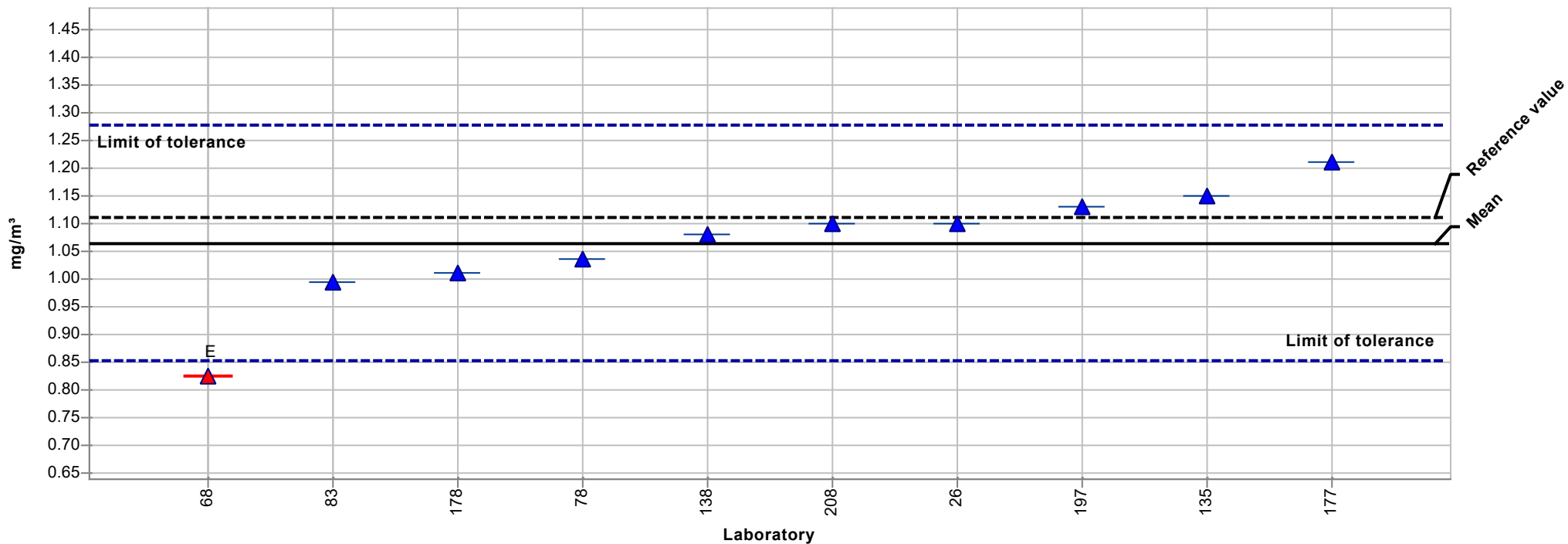
Summary results

Sample:	1	Mean:	2.389 mg/m ³
Measurand:	nitric acid	Reproducibility s.d.:	0.115 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	4.80%
Rel. target s.d.:	10.00%	Reference value:	2.340 mg/m ³
Number of laboratories in calculation + outliers:	10	Range of tolerance:	1.911 - 2.867 mg/m ³ (Z-Score ≤ 2.00)



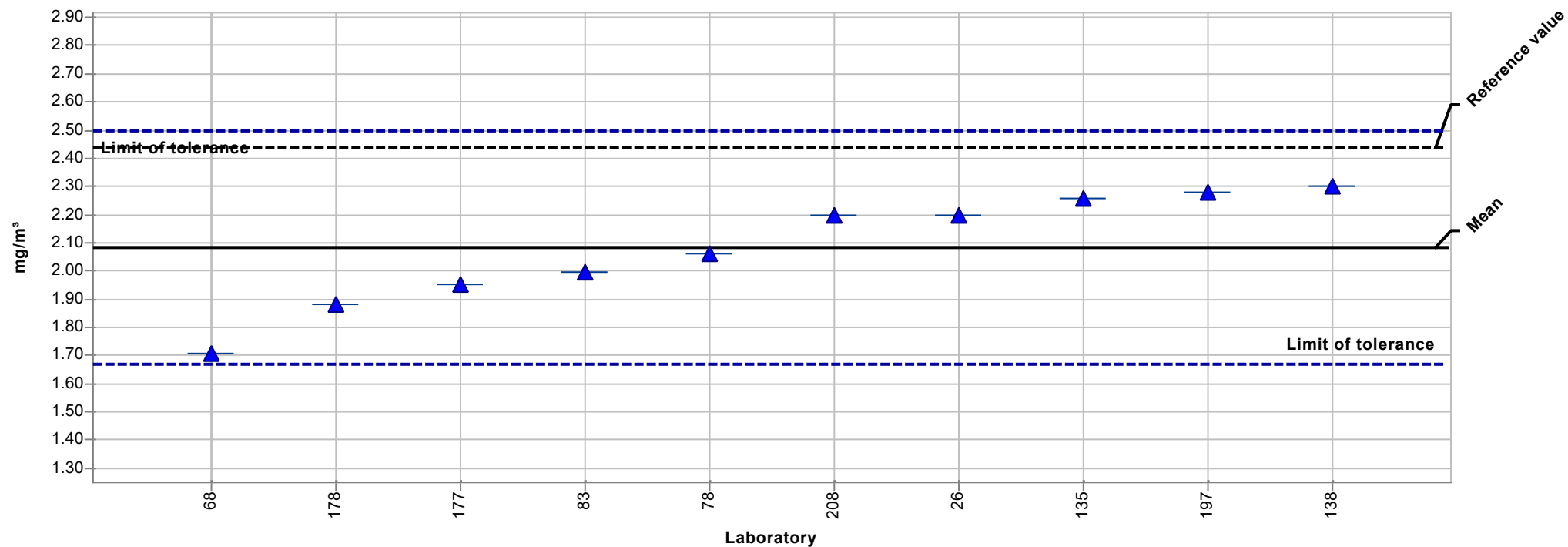
Summary results

Sample:	2	Mean:	1.064 mg/m ³
Measurand:	nitric acid	Reproducibility s.d.:	0.106 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	10.00%
Rel. target s.d.:	10.00%	Reference value:	1.110 mg/m ³
Number of laboratories in calculation:	10	Range of tolerance:	0.851 - 1.276 mg/m ³ (Z-Score ≤ 2.00)



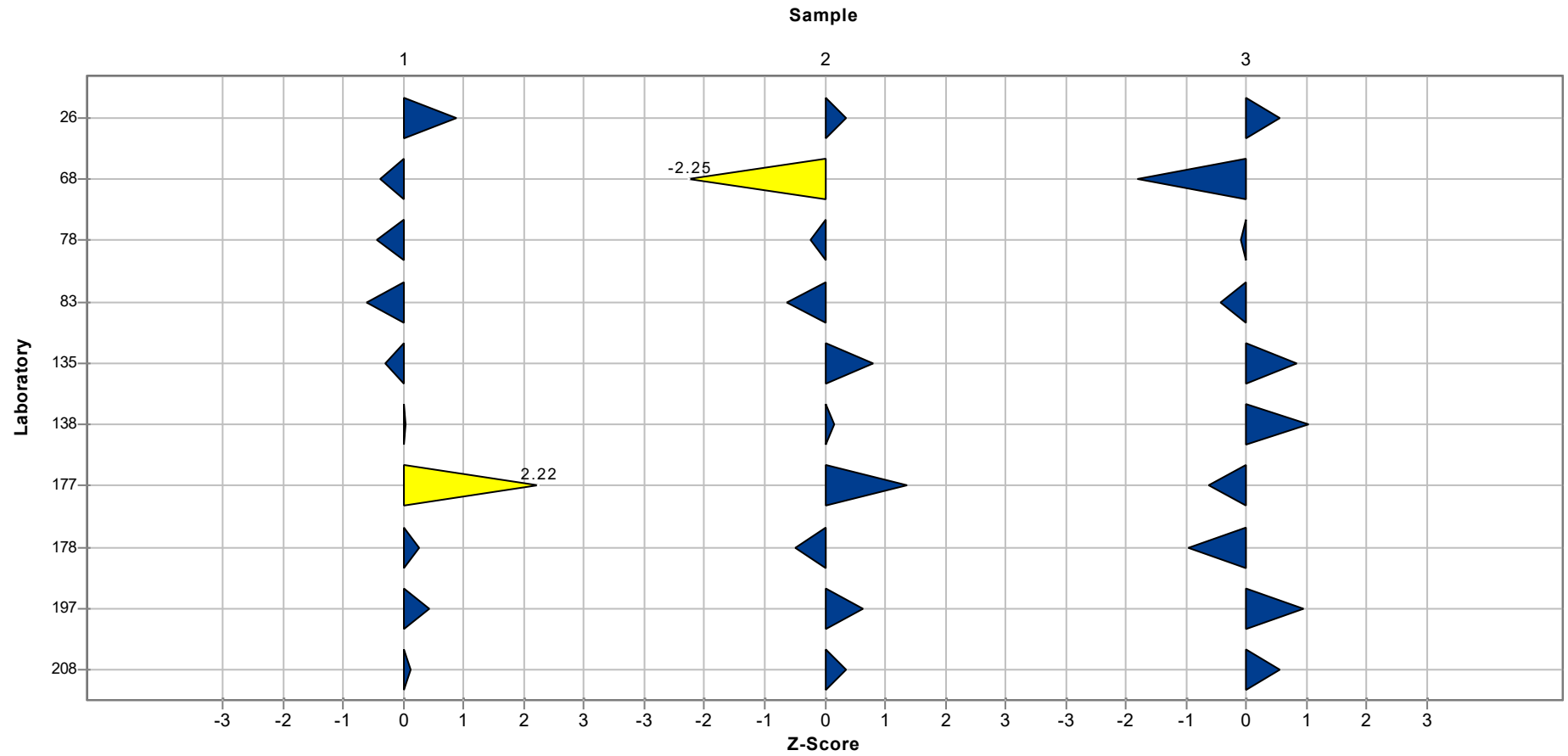
Summary results

Sample:	3	Mean:	2.083 mg/m ³
Measurand:	nitric acid	Reproducibility s.d.:	0.198 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	9.51%
Rel. target s.d.:	10.00%	Reference value:	2.440 mg/m ³
Number of laboratories in calculation:	10	Range of tolerance:	1.667 - 2.500 mg/m ³ (Z-Score ≤ 2.00)



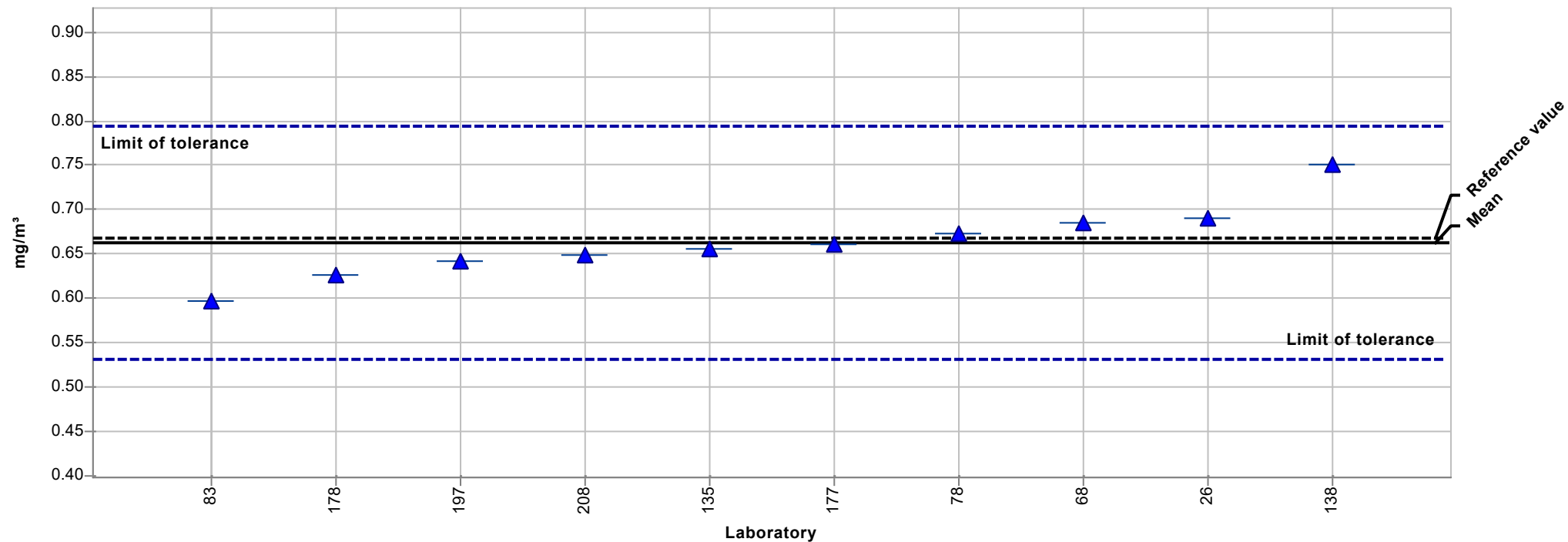
Analyte chart of Z-Scores

Measurand: nitric acid



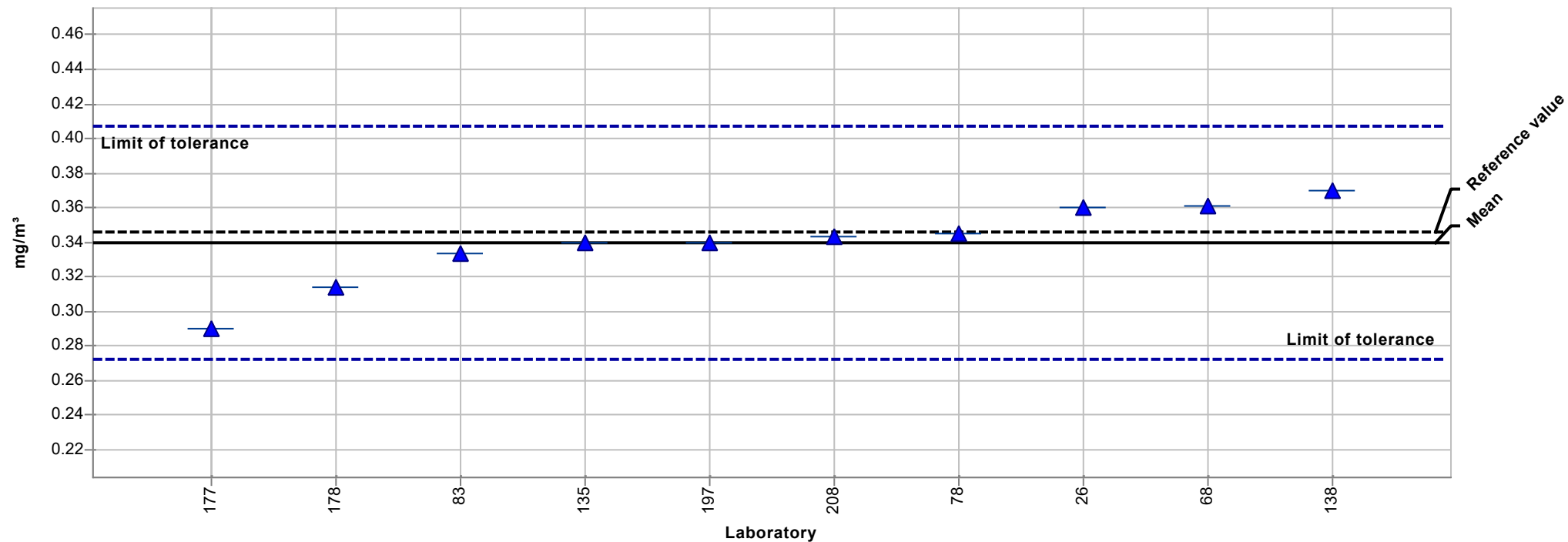
Summary results

Sample:	1	Mean:	0.662 mg/m ³
Measurand:	phosphoric acid	Reproducibility s.d.:	0.041 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	6.26%
Rel. target s.d.:	10.00%	Reference value:	0.668 mg/m ³
Number of laboratories in calculation:	10	Range of tolerance:	0.530 - 0.795 mg/m ³ (Z-Score ≤ 2.00)



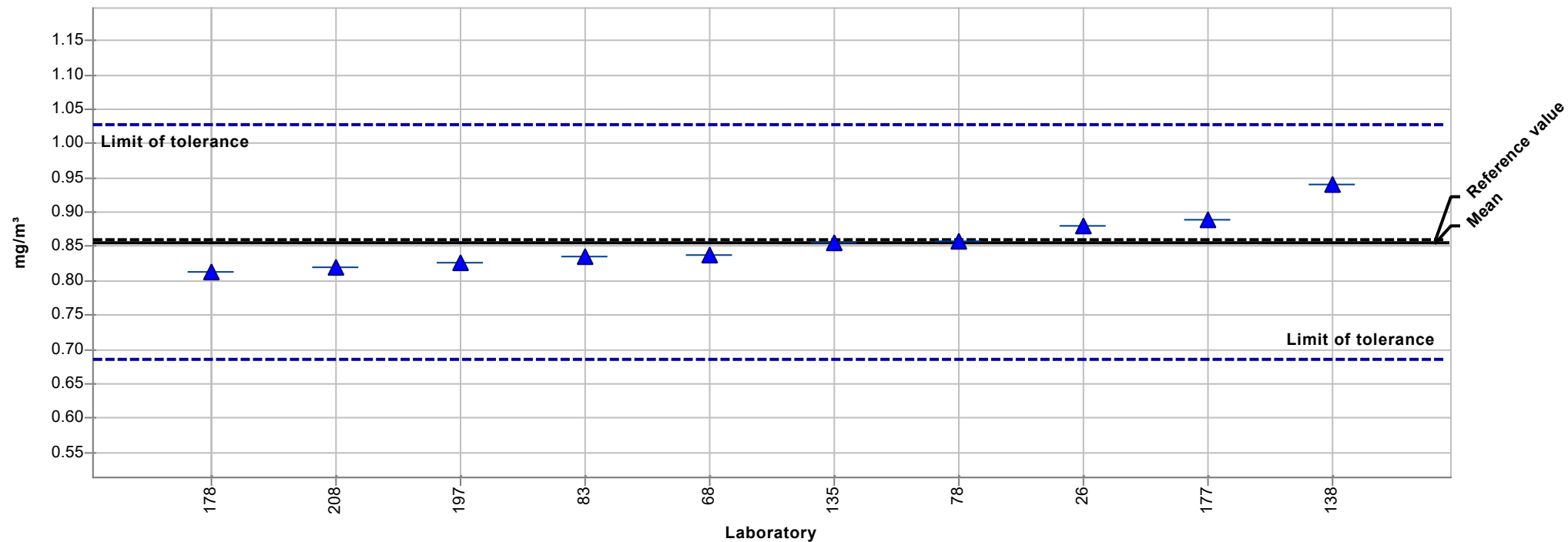
Summary results

Sample:	2	Mean:	0.340 mg/m ³
Measurand:	phosphoric acid	Reproducibility s.d.:	0.024 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	6.93%
Rel. target s.d.:	10.00%	Reference value:	0.346 mg/m ³
Number of laboratories in calculation:	10	Range of tolerance:	0.272 - 0.408 mg/m ³ (Z-Score ≤ 2.00)



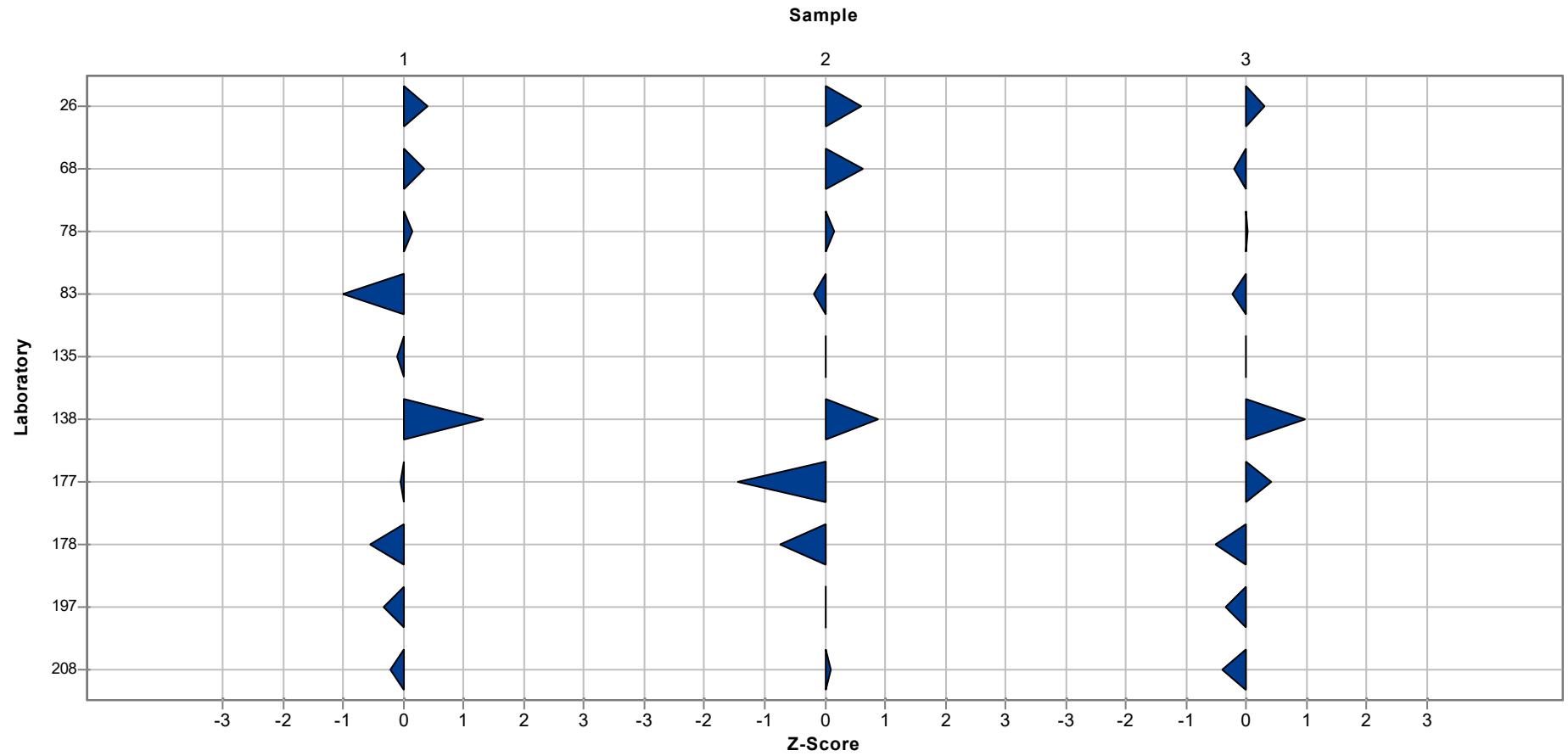
Summary results

Sample:	3	Mean:	0.855 mg/m ³
Measurand:	phosphoric acid	Reproducibility s.d.:	0.039 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	4.55%
Rel. target s.d.:	10.00%	Reference value:	0.860 mg/m ³
Number of laboratories in calculation:	10	Range of tolerance:	0.684 - 1.027 mg/m ³ (Z-Score ≤ 2.00)



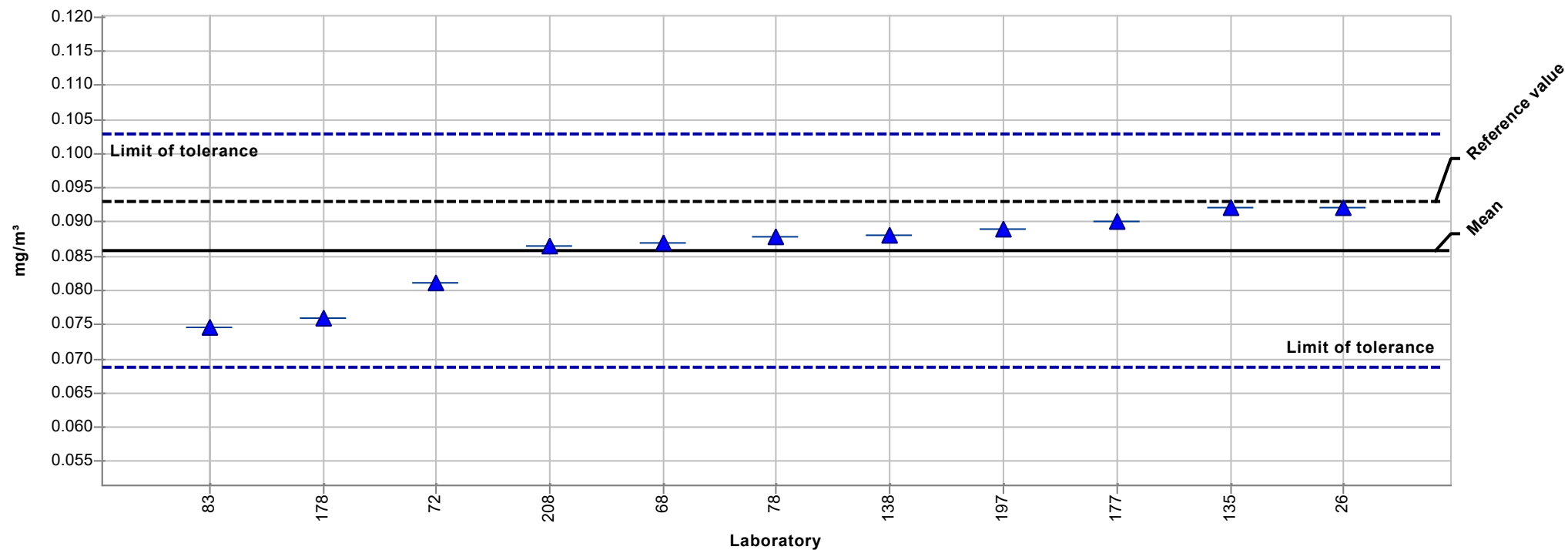
Analyte chart of Z-Scores

Measurand: phosphoric acid



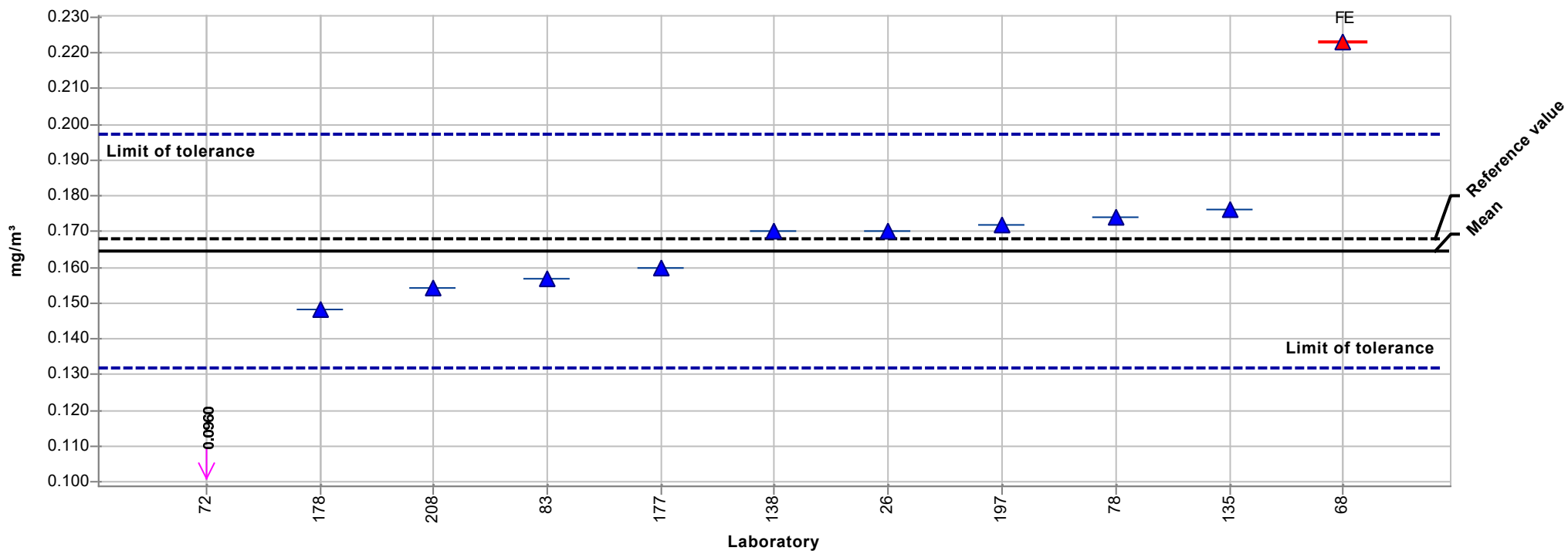
Summary results

Sample:	1	Mean:	0.0858 mg/m ³
Measurand:	sulphuric acid	Reproducibility s.d.:	0.0060 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	7.00%
Rel. target s.d.:	10.00%	Reference value:	0.0930 mg/m ³
Number of laboratories in calculation:	11	Range of tolerance:	0.0687 - 0.1030 mg/m ³ (Z-Score <= 2.00)



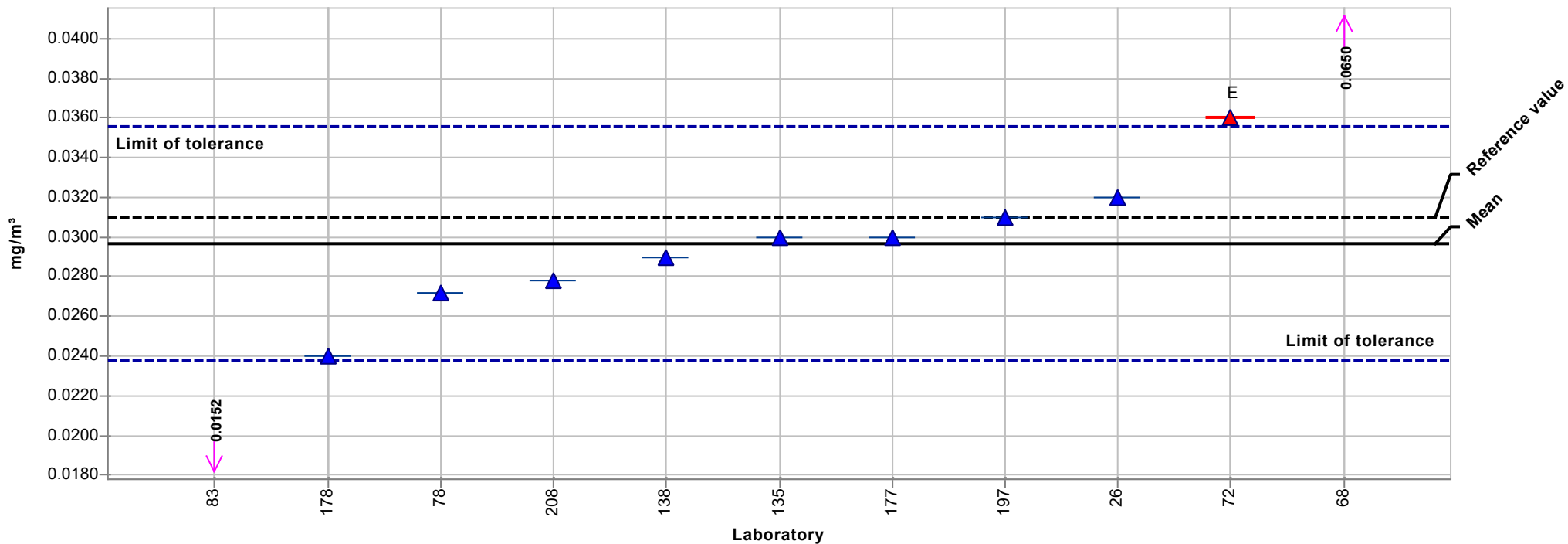
Summary results

Sample:	2	Mean:	0.1645 mg/m ³
Measurand:	sulphuric acid	Reproducibility s.d.:	0.0100 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	6.09%
Rel. target s.d.:	10.00%	Reference value:	0.1680 mg/m ³
Number of laboratories in calculation:	9	Range of tolerance:	0.1316 - 0.1974 mg/m ³ (Z-Score <= 2.00)



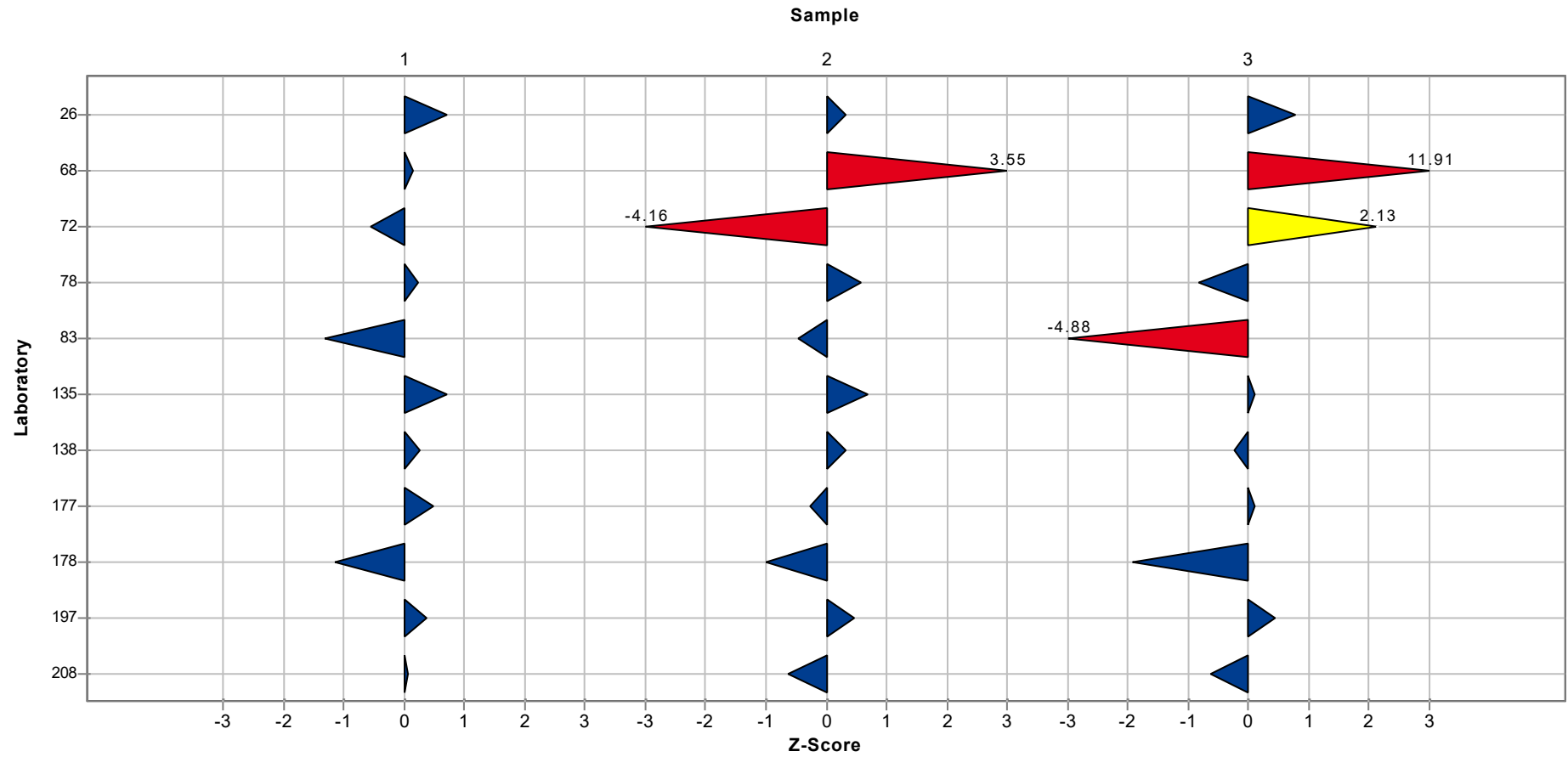
Summary results

Sample:	3	Mean:	0.0297 mg/m ³
Measurand:	sulphuric acid	Reproducibility s.d.:	0.0033 mg/m ³
Method:	ISO 5725-2	Rel. reproducibility s.d.:	11.29%
Rel. target s.d.:	10.00%	Reference value:	0.0310 mg/m ³
Number of laboratories in calculation + outliers:	11	Range of tolerance:	0.0237 - 0.0356 mg/m ³ (Z-Score <= 2.00)



Analyte chart of Z-Scores

Measurand: sulphuric acid



Questions and Answers

Participant	Analytical method	Desorption solution
26	IFA 6172 und IFA 6173	Reinstw asser bzw . Eluent
68	IFA-Arbeitsmappe	Impr. QFF: Wasser / Desorb. QFF: 3.6mM Natriumcarbonat-Lsg.
72	H2SO4/H3PO4: AA.EZM/I.45.03	HH3PO4/H2SO4 Direktinjektion aus Pufferlsg.
78		Wasser
83	NF X43-281 et NF EN ISO 10304	Water 18.2
135	IFA 6172, IFA 6173	Reinstw asser 18,2MOhm
138	IFA 6172 + 6173	Reinstw asser
177	IFA-Arbeitsmappe	Reinstw asser
178	MTA/MA-019/A90 ; MTA/MA 60/A05	Water
197	IFA 6172/IFA 6173	NaHCO3/Na2CO3
208	Ion chromatography w ith conductivity detector	UHP w ater

Participant	Volume of desorption solution	Time of desorption
26	30 ml	15 Min Ultraschallbad
68	Impr. QFF: 10 ml / Desorb. QFF: Verdünnung von 2.5 ml Desorptionslg./10 ml	15 Min. Ultraschallbad, anschl. mind. 30 Min. stehen lassen
78	10 mL	30 min Ultraschall
83	30 mL	30 minutes
135	10	15 min Ultraschallbad, 30 min Standzeit
138	10 bzw . 4 ml	15 Minuten im Ultraschallbad, 30 Minuten stehen lassen
177	20 ml	30 Minuten Ultraschall
178	10 ml	15 min
197	20	U-Bad 15 min + 30 min stehenlassen
208	10 mL	45 min, ultrasonic bath used

Participant	Ion Chromatographic System	Analytical column
26	Peristaltikpumpe, Leitfähigkeitsdetektor, Metrohm Autosampler	Metrosep A Supp 5 - 150/4.0

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Participant	Ion Chromatographic System	Analytical column
68	930 Compact IC Flex von Metrohm	Metrosep C 6 - 250/4.0 von Metrohm
72	Dionex ICS 2000, Leitfähigkeitsdetektor	Dionex Ionpac AS11-HC 2x 250 mm
78	Metrohm IC	Metrosep A Supp 5 250 mm
83	Conductivity detector	AS9HC, AS11HC and CS16
135	Dionex ICS-2100, AS-Autosampler	Vorsäule AG15, Trennsäule AS15
138	Dionex ICS 1100	Dionex IonPac AS22 4*250 MM
177	Dionex ICS 2000	AS15
178	conductivity detector	Metrosep A Supp 5 - 150/4,0
197	Metrohm: 861 Compact IC, 838 Sampler, LF-Detektor, Doppelkolbenhochdruckpumpe	Metrosep S Supp5
208	Dionex ICS-5000 dual pump system	Dionex IonPac AS11-HC-4µm

Participant	Mobile phase	Flow rate	Recovery rate
26	Natriumhydrogencarbonat: 1,7 mmol/L Natriumcarbonat: 1,8 mmol/L Oxalsäure: 0,004 mmol/L	0,7	nein
68	3.6 mM Natriumcarbonat-Lsg.	0.7 ml/min.	Nein
72	30 mmol KOH	0,38 ml/min	
78	3,2 mmol/L Natriumcarbonat & 1,0 mmol/L Natriumhydrogencarbonat	0,7 mL/min	
83	KOH, Na2CO3 end Methanesulfonic Acid	1 mL/min	No
135	Kaliumhydroxid Gradient zw . 30-45mmol	0,35	nein
138	Na2CO3 / NaHCO3	1,2 ml/min	
177	KOH 12-48 mmol/l	0,3 ml/min	nein
178	Carbonato sódico 3,2 mM + bicarbonato sódico 1mM	0.8	no
197	1mmol/NaHCO3/3,2 mmol/l Na2CO3	0,7	-
208	1-60 mM KOH	15 µL/min	no

Participant	Date of analysis
26	24.03.2020
68	24./25.3.2020
72	11. -15.05.2020
78	14-17.04.2020

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Participant	Date of analysis
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83	24/03/2020, 25/03/2020 and 30/03/2020
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135	Siehe Tab Messw erte
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138	16.04.2020
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177	20.05.2020
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178	23/04/2020
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197	18.3. bzw . 19.3.2020
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208	15/04/2020
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