Summary of laboratory means

Sample sample 1

Laboratory	hydrochloric acid	Z score	nitric acid	Z score	phosphoric acid	Z score	sulfuric acid	Z score
Measurement unit	mg/m³		mg/m³		mg/m³		mg/m³	
–	–	– –	–	– –	–	– –	–	– –
5	0,769	-0,333	0,464	-0,884	0,105	0,004	0,105	0,397
6	0,798	0,031	0,303	-4,047 FE	0,107	0,195	0,105	0,397
17	0,829	0,421	0,534	0,491	0,109	0,385	0,103	0,199
40	0,838	0,530	0,583	1,454	0,110	0,480	0,099	-0,207
41					0,108	0,290	0,106	0,496
102	0,721	-0,937	0,520	0,216	0,111	0,557	0,095	-0,613
111	0,869	0,924	0,508	-0,020	0,109	0,385	0,106	0,496
121	0,848	0,664	0,559	0,976	0,111	0,576	0,096	-0,494
126	0,565	-2,898 E	0,355	-3,026 E				
151	0,816	0,257	0,489	-0,403	0,104	-0,091	0,102	0,100
181	0,845	0,622	0,540	0,609	0,100	-0,472	0,100	-0,098
197	0,807	0,144	0,472	-0,727	0,076	-2,788 E	0,096	-0,465
–	–	– –	–	– –	–	– –	–	– –
Method	ISO 5725		ISO 5725		ISO 5725		ISO 5725	
Assessment	|Z|<=2,000		|Z|<=2,000		|Z|<=2,000		|Z|<=2,000	
Mean	0,796		0,509		0,105		0,101	
Reproducibility s.d.	0,089		0,075		0,010		0,004	
Rel. reproducibility s.d.	11,23 %		14,68 %		9,39 %		4,07 %	
Reference value	0,834		0,563		0,100		0,104	
Rel. target s.d.	10,00 %		10,00 %		10,00 %		10,00 %	
Low er limit of tolerance	0,636		0,407		0,084		0,081	
Upper limit of tolerance	0,955		0,611		0,126		0,121	
Low er confidence limit	0,744		0,465		0,099		0,099	
Upper confidence limit	0,847		0,553		0,111		0,103	

Ringversuch inorganic acids with sampling

Laboratory	hydrochloric acid	Z score	nitric acid	Z score	phosphoric acid	Z score	sulfuric acid	Z score
Type B outliers	0		0		0		0	
Type F outliers	0		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)	11		10		11		11	

Explanation of outlier types

A: Single outlier

B: Differing laboratory mean

C: Excluded lab due to s.d.

D: Excluded manually

E: |Score|>Tol.

F: |Score|>3,5

Summary of laboratory means

Sample sample 2

Laboratory	hydrochloric acid	Z score	nitric acid	Z score	phosphoric acid	Z score	sulfuric acid	Z score
Measurement unit	mg/m³		mg/m³		mg/m³		mg/m³	
–	–	– –	–	– –	–	– –	–	– –
5	1,820	-0,103	1,040	-0,999	0,326	-0,160	0,034	5,564 BE
6	1,808	-0,169	0,727	-3,708 FE	0,340	0,262	0,023	0,529
17	1,866	0,147	1,167	0,100	0,339	0,232	0,028	2,863 E
40	1,958	0,647	1,289	1,156	0,325	-0,186	0,021	-0,479
41					0,326	-0,160	0,021	-0,387
102	1,801	-0,207	1,242	0,749	0,355	0,718	0,021	-0,250
111	2,007	0,914	1,235	0,689	0,337	0,172	0,025	1,444
121	1,959	0,654	1,239	0,726	0,324	-0,221	0,020	-0,845
126	1,505	-1,816	0,960	-1,691				
151	1,884	0,245	1,087	-0,597	0,327	-0,130	0,021	-0,387
181	1,930	0,495	1,215	0,516	0,320	-0,341	0,020	-0,845
197	1,717	-0,665	1,054	-0,881	0,179	-4,597 BE	0,019	-1,165
–	–	– –	–	– –	–	– –	–	– –
Method	ISO 5725		ISO 5725		ISO 5725		ISO 5725	
Assessment	|Z|<=2,000		|Z|<=2,000		|Z|<=2,000		|Z|<=2,000	
Mean	1,839		1,155		0,331		0,022	
Reproducibility s.d.	0,146		0,121		0,010		0,003	
Rel. reproducibility s.d.	7,94 %		10,45 %		3,15 %		12,05 %	
Reference value	1,907		1,217		0,324		0,024	
Rel. target s.d.	10,00 %		10,00 %		10,00 %		10,00 %	
Low er limit of tolerance	1,471		0,924		0,265		0,017	
Upper limit of tolerance	2,207		1,387		0,398		0,026	
Low er confidence limit	1,752		1,082		0,325		0,020	
Upper confidence limit	1,926		1,229		0,338		0,024	

Ringversuch inorganic acids with sampling

Laboratory	hydrochloric acid	Z score	nitric acid	Z score	phosphoric acid	Z score	sulfuric acid	Z score
Type B outliers	0		0		1		1	
Type F outliers	0		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)	11		10		10		10	

Explanation of outlier types

A: Single outlier

B: Differing laboratory mean

C: Excluded lab due to s.d.

D: Excluded manually

E: |Score|>Tol.

F: |Score|>3,5

Summary of laboratory means

Sample sample 3

Laboratory	hydrochloric acid	Z score	nitric acid	Z score	phosphoric acid	Z score	sulfuric acid	Z score
Measurement unit	mg/m³		mg/m³		mg/m³		mg/m³	
–	–	– –	–	– –	–	– –	–	– –
5	4,270	0,131	3,470	-0,638	0,610	-0,372	0,064	0,667
6	4,303	0,209	2,326	-3,724 BE	0,643	0,149	0,060	0,000
17	4,298	0,197	3,855	0,401	0,677	0,686	0,061	0,150
40	4,514	0,710	4,280	1,547	0,622	-0,179	0,057	-0,467
41					0,616	-0,277	0,058	-0,333
102	3,887	-0,778	3,833	0,341	0,646	0,190	0,069	1,450
111	4,729	1,220	3,536	-0,460	0,648	0,228	0,063	0,500
121	4,566	0,834	4,154	1,206	0,626	-0,119	0,053	-1,167
126	3,475	-1,755	3,270	-1,178				
151	4,252	0,088	3,718	0,030	0,639	0,086	0,058	-0,333
181	4,443	0,542	3,813	0,288	0,620	-0,214	0,060	0,000
197	3,883	-0,787	3,247	-1,240	0,070	-8,897 BE	0,015	-7,467 BE
–	–	– –	–	– –	–	– –	–	– –
Method	ISO 5725		ISO 5725		ISO 5725		ISO 5725	
Assessment	|Z|<=2,000		|Z|<=2,000		|Z|<=2,000		|Z|<=2,000	
Mean	4,215		3,706		0,634		0,060	
Reproducibility s.d.	0,383		0,385		0,019		0,004	
Rel. reproducibility s.d.	9,09 %		10,40 %		3,07 %		7,03 %	
Reference value	4,389		3,981		0,610		0,062	
Rel. target s.d.	10,00 %		10,00 %		10,00 %		10,00 %	
Low er limit of tolerance	3,372		2,965		0,507		0,048	
Upper limit of tolerance	5,058		4,448		0,760		0,072	
Low er confidence limit	3,989		3,471		0,621		0,057	
Upper confidence limit	4,441		3,942		0,646		0,063	

Ringversuch inorganic acids with sampling

Laboratory	hydrochloric acid	Z score	nitric acid	Z score	phosphoric acid	Z score	sulfuric acid	Z score
Type B outliers	0		1		1		1	
Type F outliers	0		0		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)	11		10		10		10	

Explanation of outlier types

A: Single outlier

B: Differing laboratory mean

C: Excluded lab due to s.d.

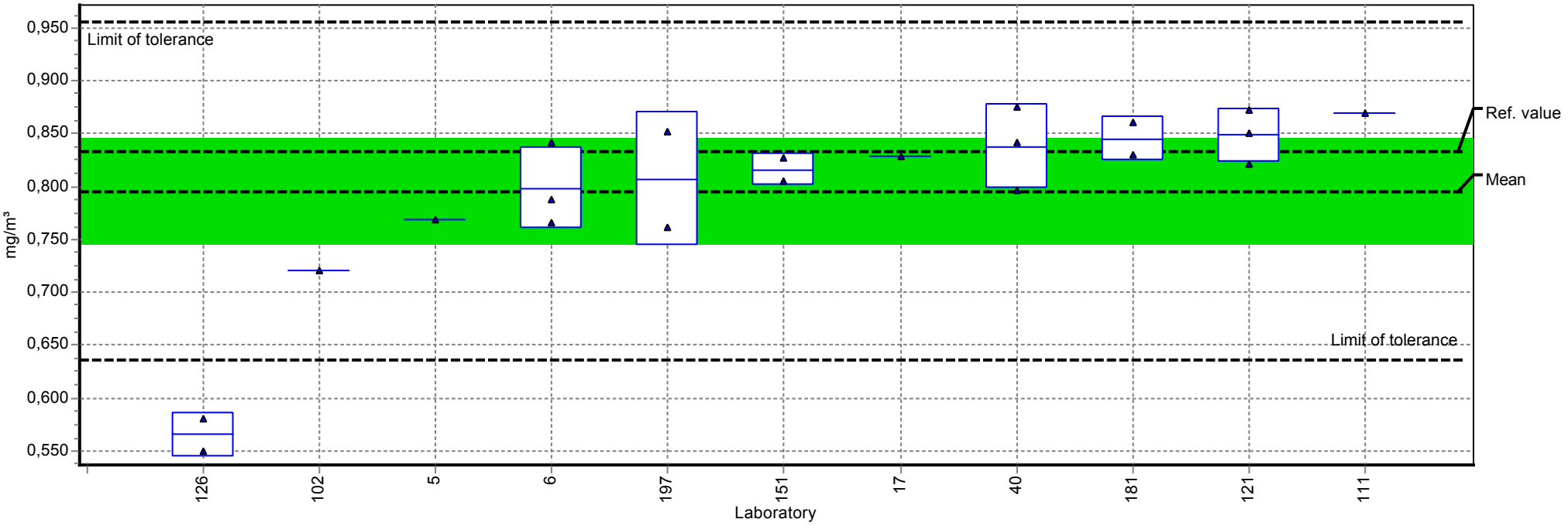
D: Excluded manually

E: |Score|>Tol.

F: |Score|>3,5

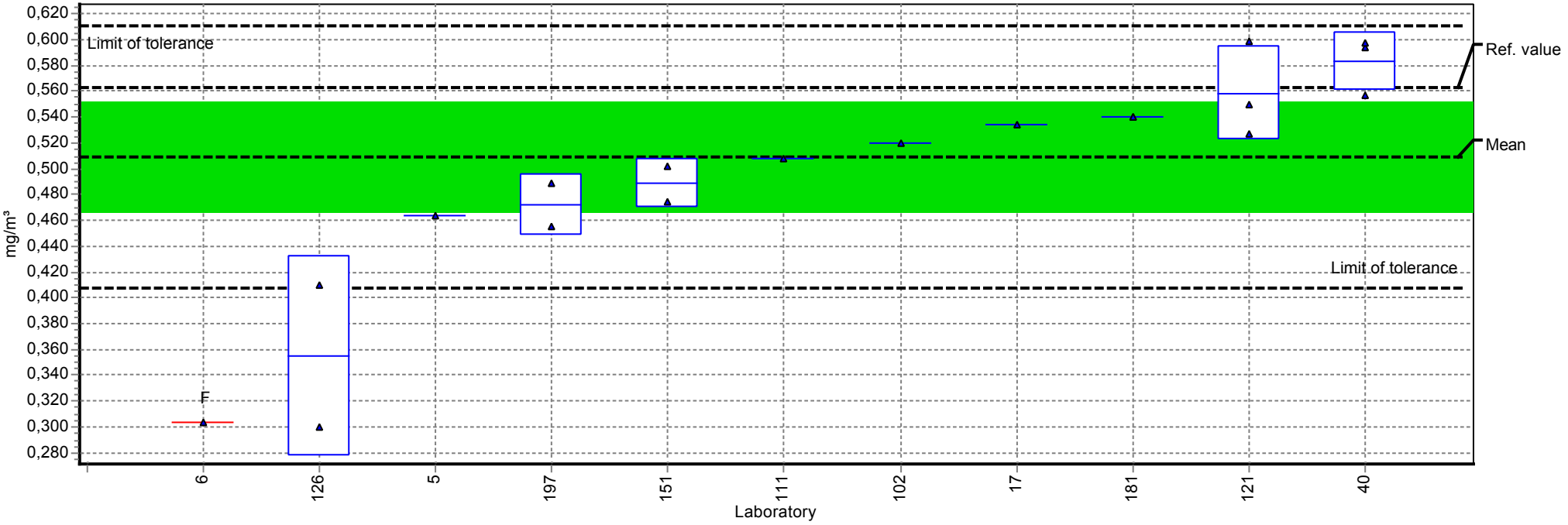
Summary results

Sample:	**sample 1**	**Mean:**	**0,796 mg/m³**
Measurand:	**hydrochloric acid**	**Reproducibility s.d.:**	**0,089 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**11,23%**
No. of laboratories:	**11**	**Tolerance limits:**	**0,636 - 0,955 mg/m³ (|Z score| < 2,00)**



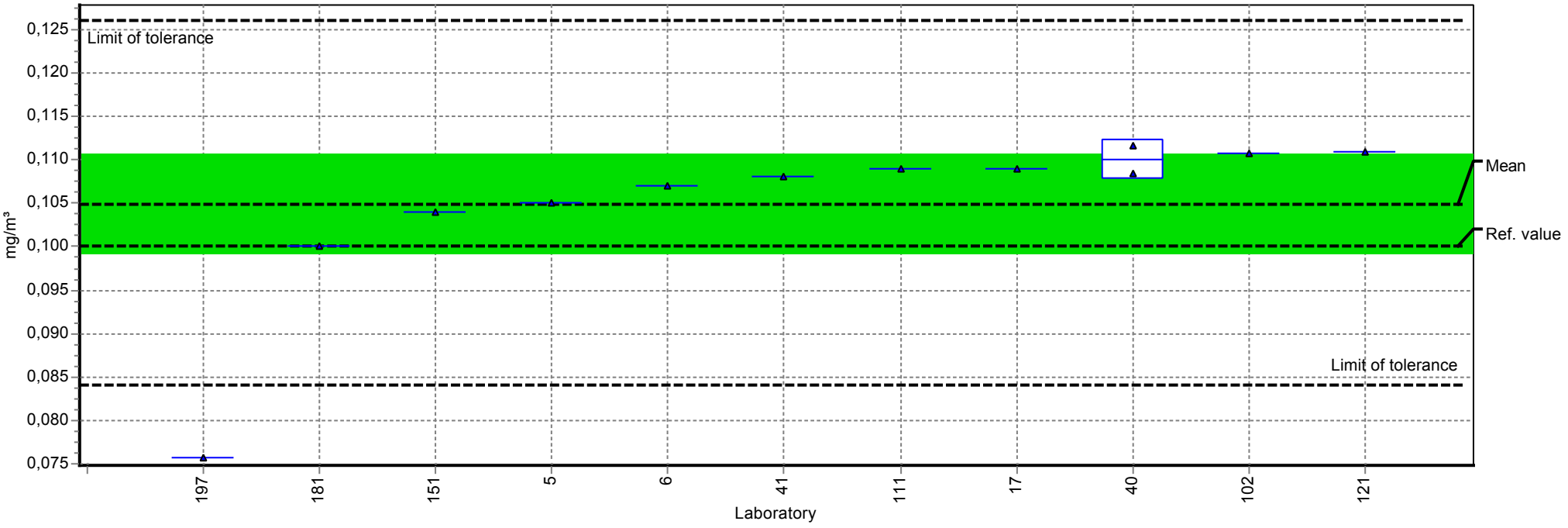
Summary results

Sample:	**sample 1**	**Mean:**	**0,509 mg/m³**
Measurand:	**nitric acid**	**Reproducibility s.d.:**	**0,075 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**14,68%**
No. of laboratories:	**10**	**Tolerance limits:**	**0,407 - 0,611 mg/m³ (|Z score| < 2,00)**



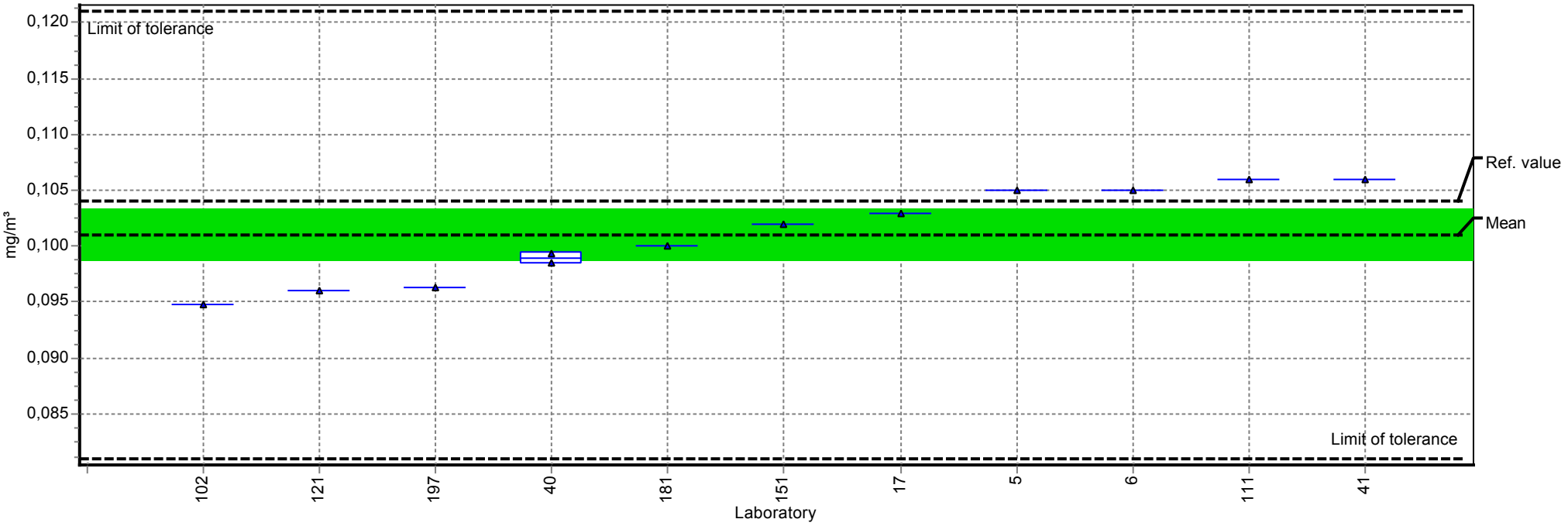
Summary results

Sample:	**sample 1**	**Mean:**	**0,105 mg/m³**
Measurand:	**phosphoric acid**	**Reproducibility s.d.:**	**0,010 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**9,39%**
No. of laboratories:	**11**	**Tolerance limits:**	**0,084 - 0,126 mg/m³ (|Z score| < 2,00)**



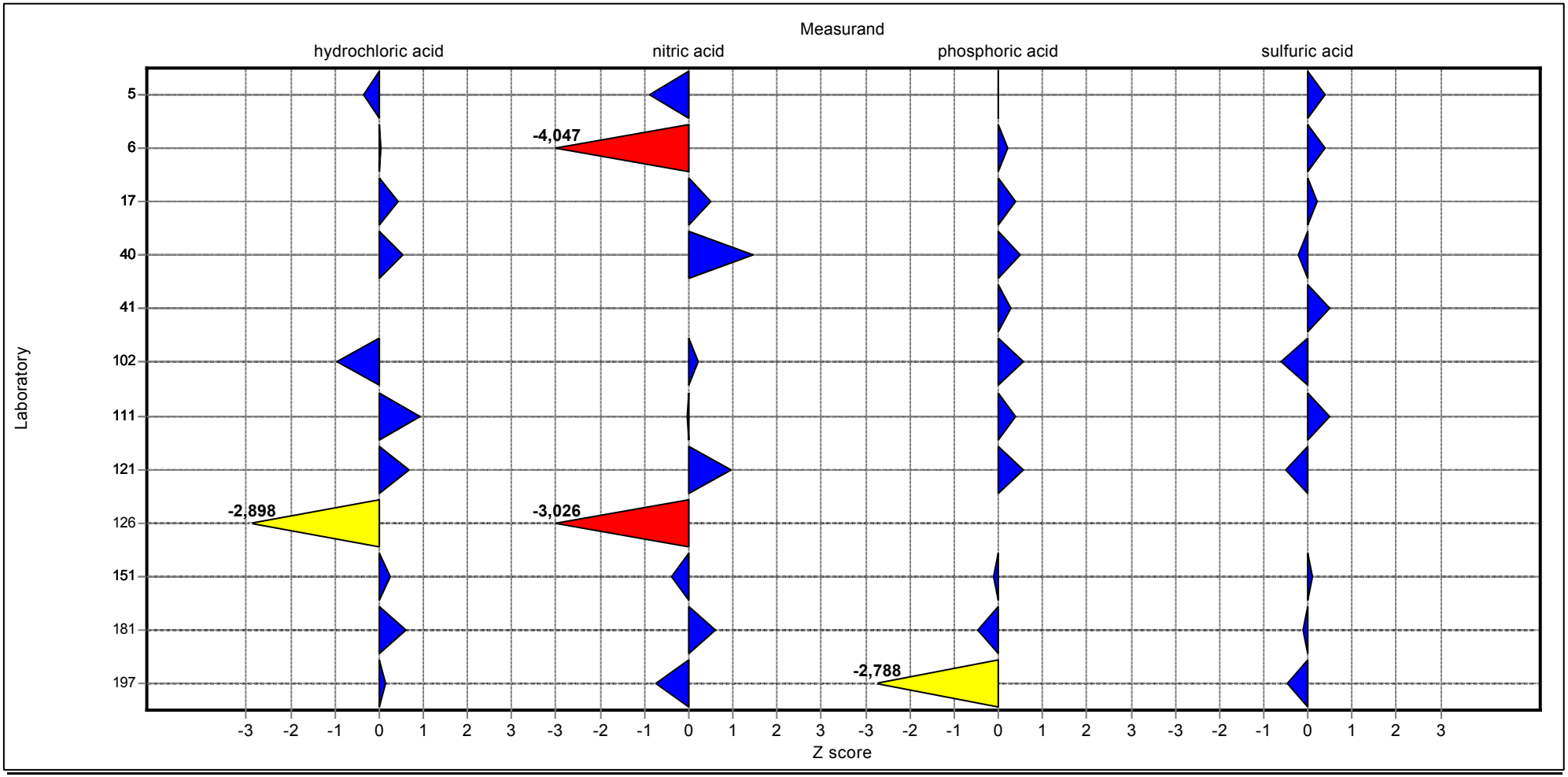
Summary results

Sample:	**sample 1**	**Mean:**	**0,101 mg/m³**
Measurand:	**sulfuric acid**	**Reproducibility s.d.:**	**0,004 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**4,07%**
No. of laboratories:	**11**	**Tolerance limits:**	**0,081 - 0,121 mg/m³ (|Z score| < 2,00)**



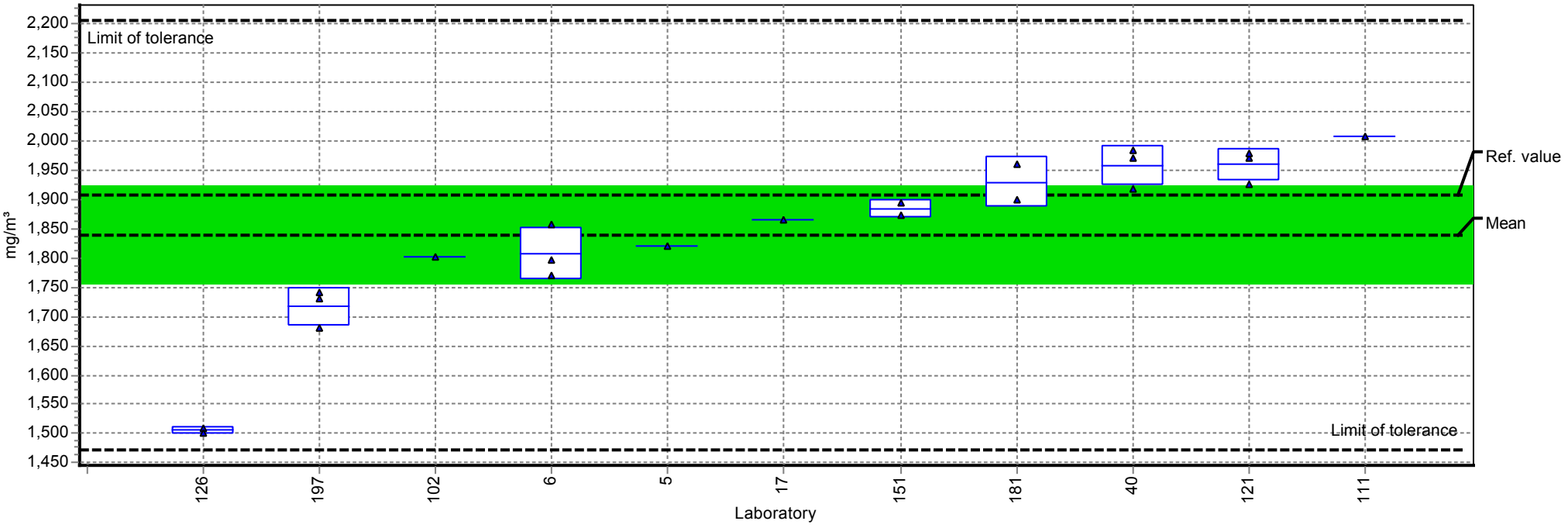
Sample chart of Z scores

Sample: sample 1



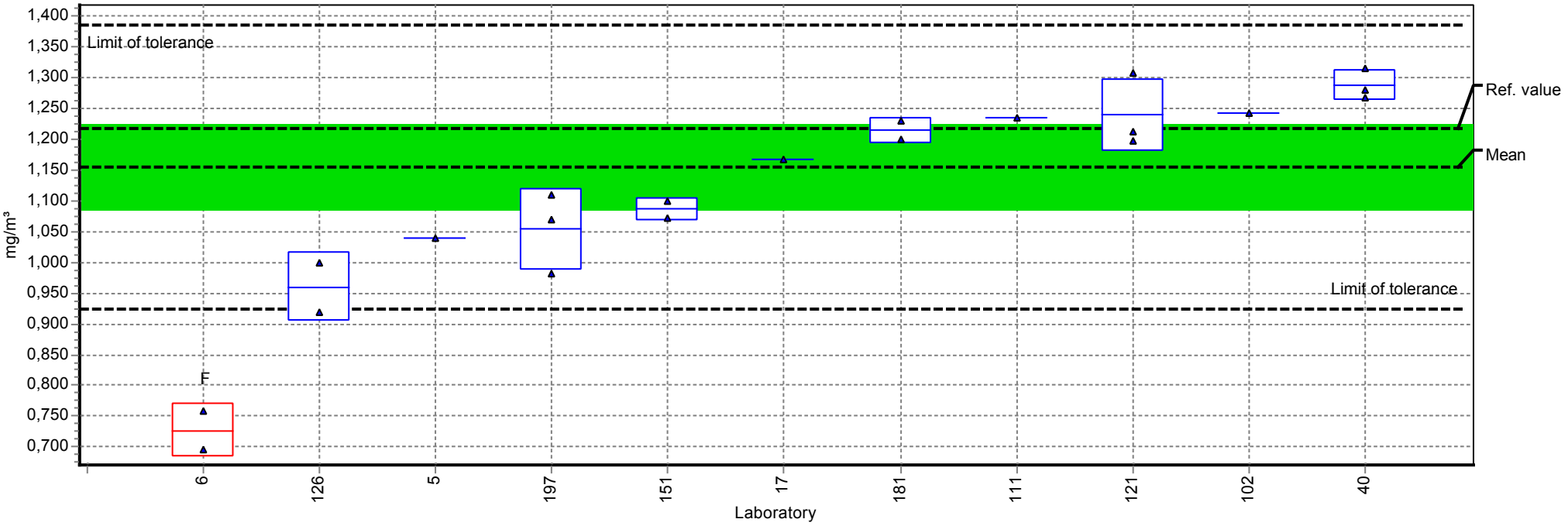
Summary results

Sample:	**sample 2**	**Mean:**	**1,839 mg/m³**
Measurand:	**hydrochloric acid**	**Reproducibility s.d.:**	**0,146 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**7,94%**
No. of laboratories:	**11**	**Tolerance limits:**	**1,471 - 2,207 mg/m³ (|Z score| < 2,00)**



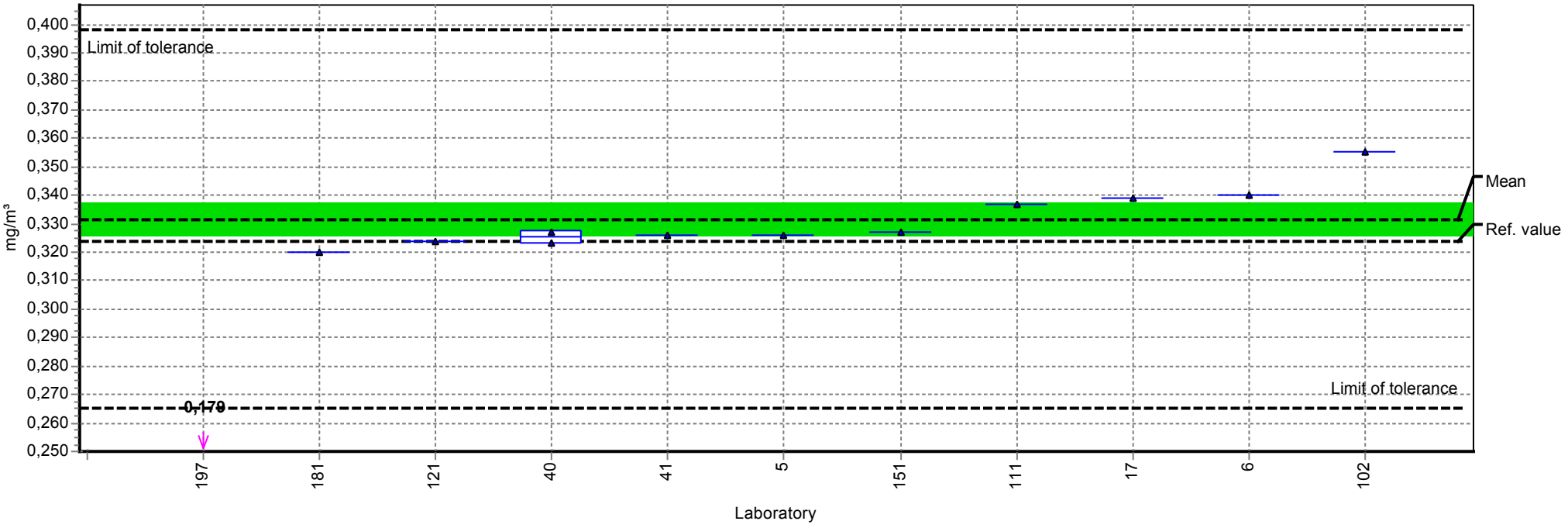
Summary results

Sample:	**sample 2**	**Mean:**	**1,155 mg/m³**
Measurand:	**nitric acid**	**Reproducibility s.d.:**	**0,121 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**10,45%**
No. of laboratories:	**10**	**Tolerance limits:**	**0,924 - 1,387 mg/m³ (|Z score| < 2,00)**



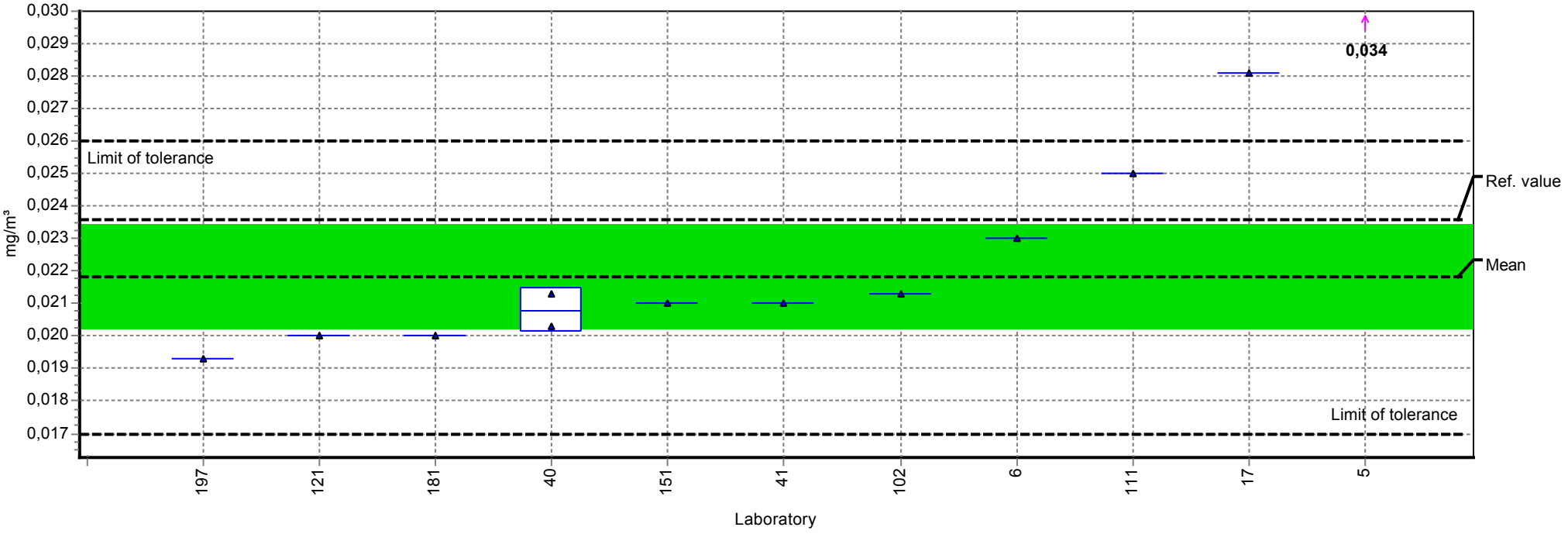
Summary results

Sample:	**sample 2**	**Mean:**	**0,331 mg/m³**
Measurand:	**phosphoric acid**	**Reproducibility s.d.:**	**0,010 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**3,15%**
No. of laboratories:	**10**	**Tolerance limits:**	**0,265 - 0,398 mg/m³ (|Z score| < 2,00)**



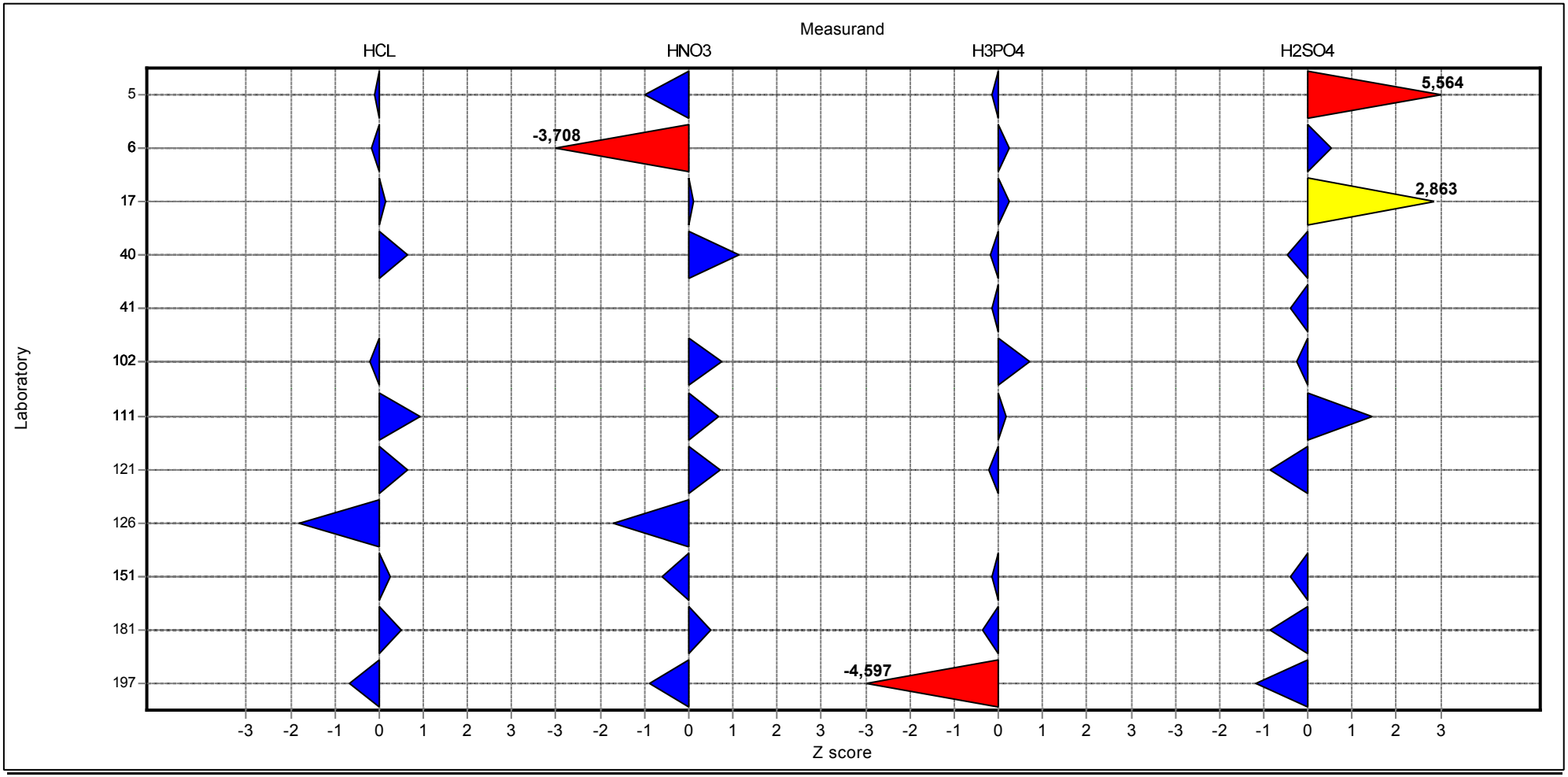
Summary results

Sample:	**sample 2**	**Mean:**	**0,022 mg/m³**
Measurand:	**sulfuric acid**	**Reproducibility s.d.:**	**0,003 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**12,05%**
No. of laboratories:	**10**	**Tolerance limits:**	**0,017 - 0,026 mg/m³ (|Z score| < 2,00)**



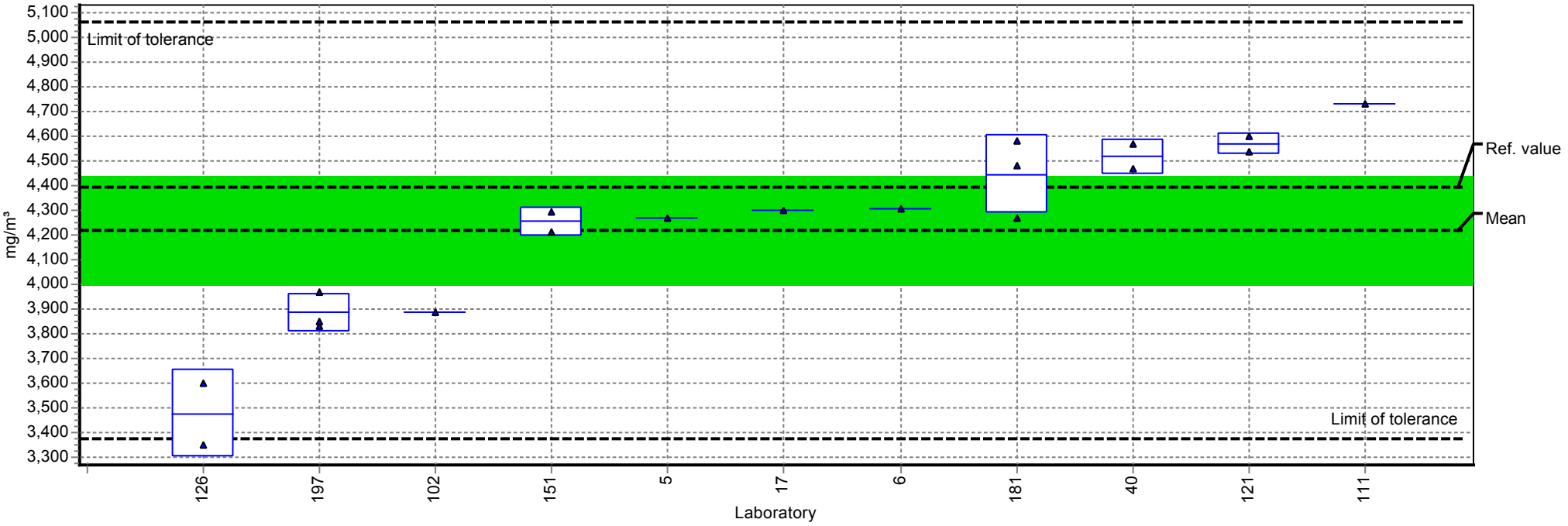
Sample chart of Z scores

Sample: sample 2



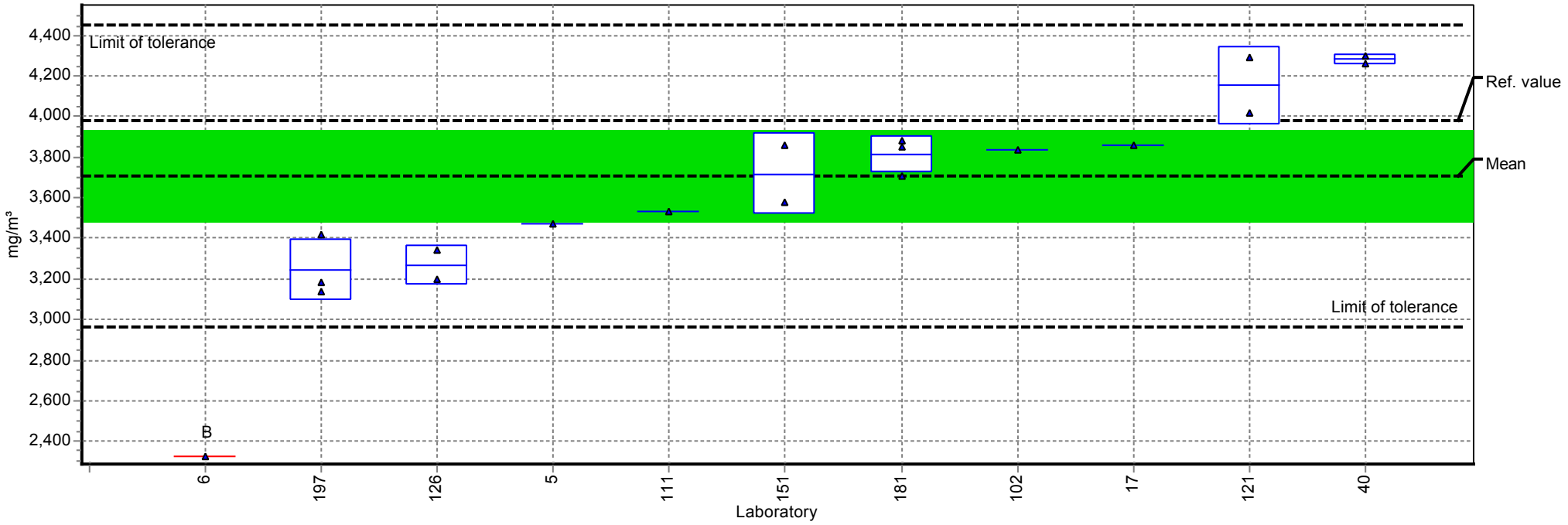
Summary results

Sample:	**sample 3**	**Mean:**	**4,215 mg/m³**
Measurand:	**hydrochloric acid**	**Reproducibility s.d.:**	**0,383 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**9,09%**
No. of laboratories:	**11**	**Tolerance limits:**	**3,372 - 5,058 mg/m³ (|Z score| < 2,00)**



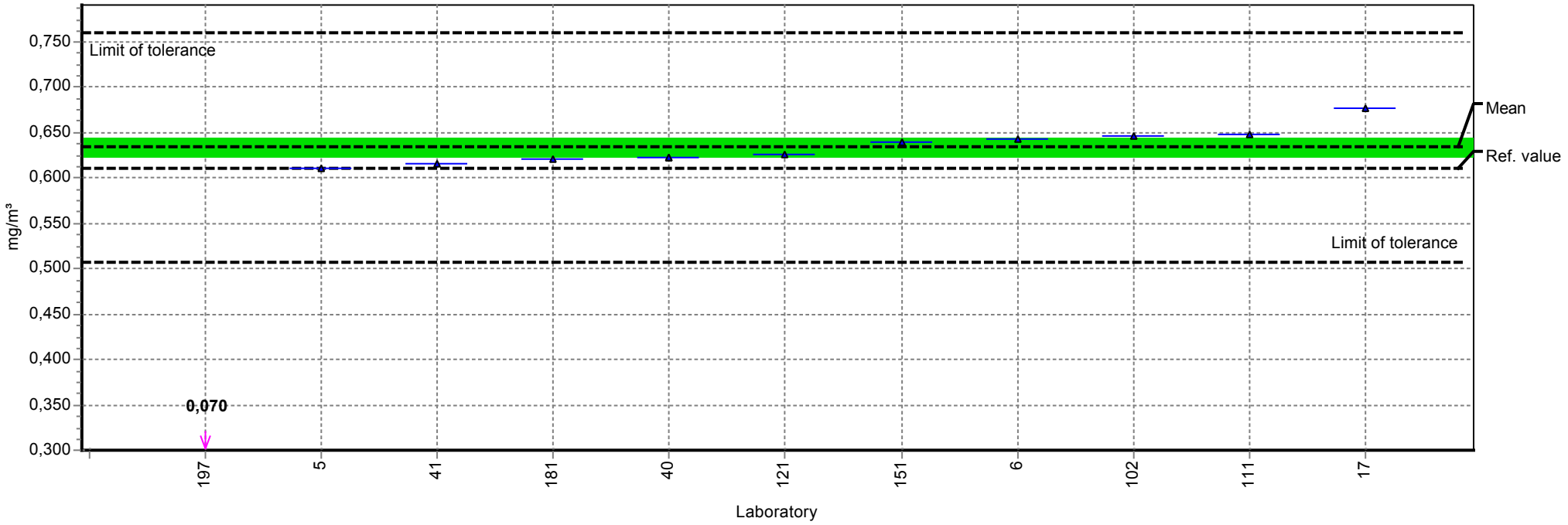
Summary results

Sample:	**sample 3**	**Mean:**	**3,706 mg/m³**
Measurand:	**nitric acid**	**Reproducibility s.d.:**	**0,385 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**10,40%**
No. of laboratories:	**10**	**Tolerance limits:**	**2,965 - 4,448 mg/m³ (|Z score| < 2,00)**



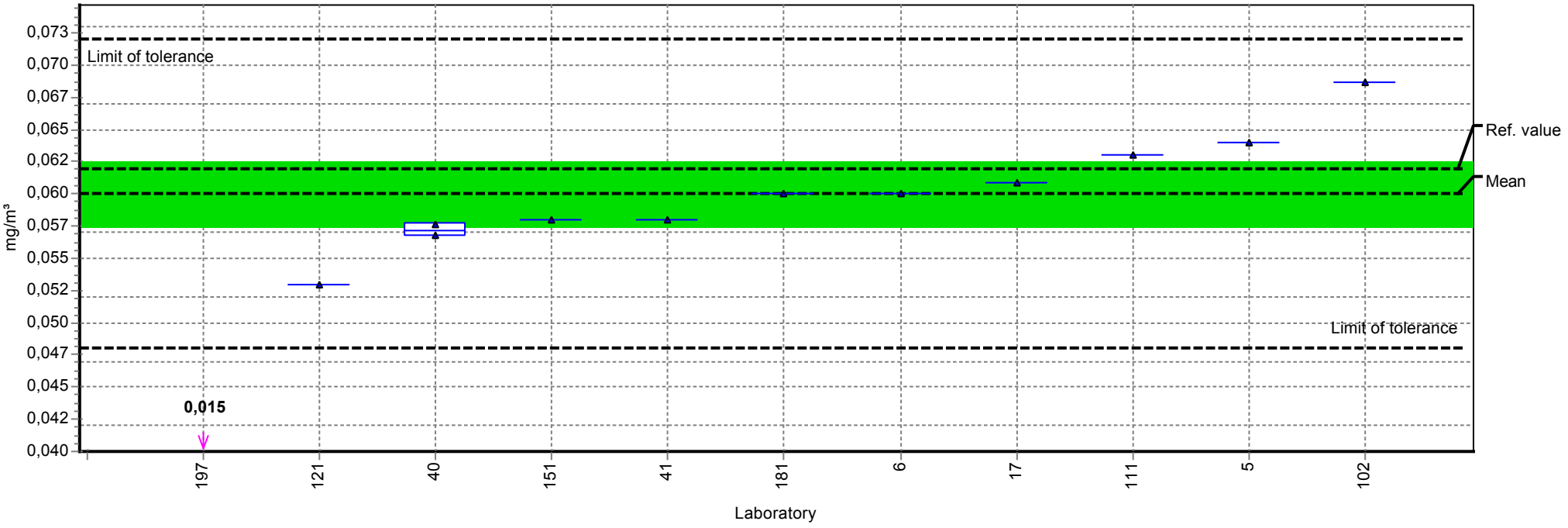
Summary results

Sample:	**sample 3**	**Mean:**	**0,634 mg/m³**
Measurand:	**phosphoric acid**	**Reproducibility s.d.:**	**0,019 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**3,07%**
No. of laboratories:	**10**	**Tolerance limits:**	**0,507 - 0,760 mg/m³ (|Z score| < 2,00)**



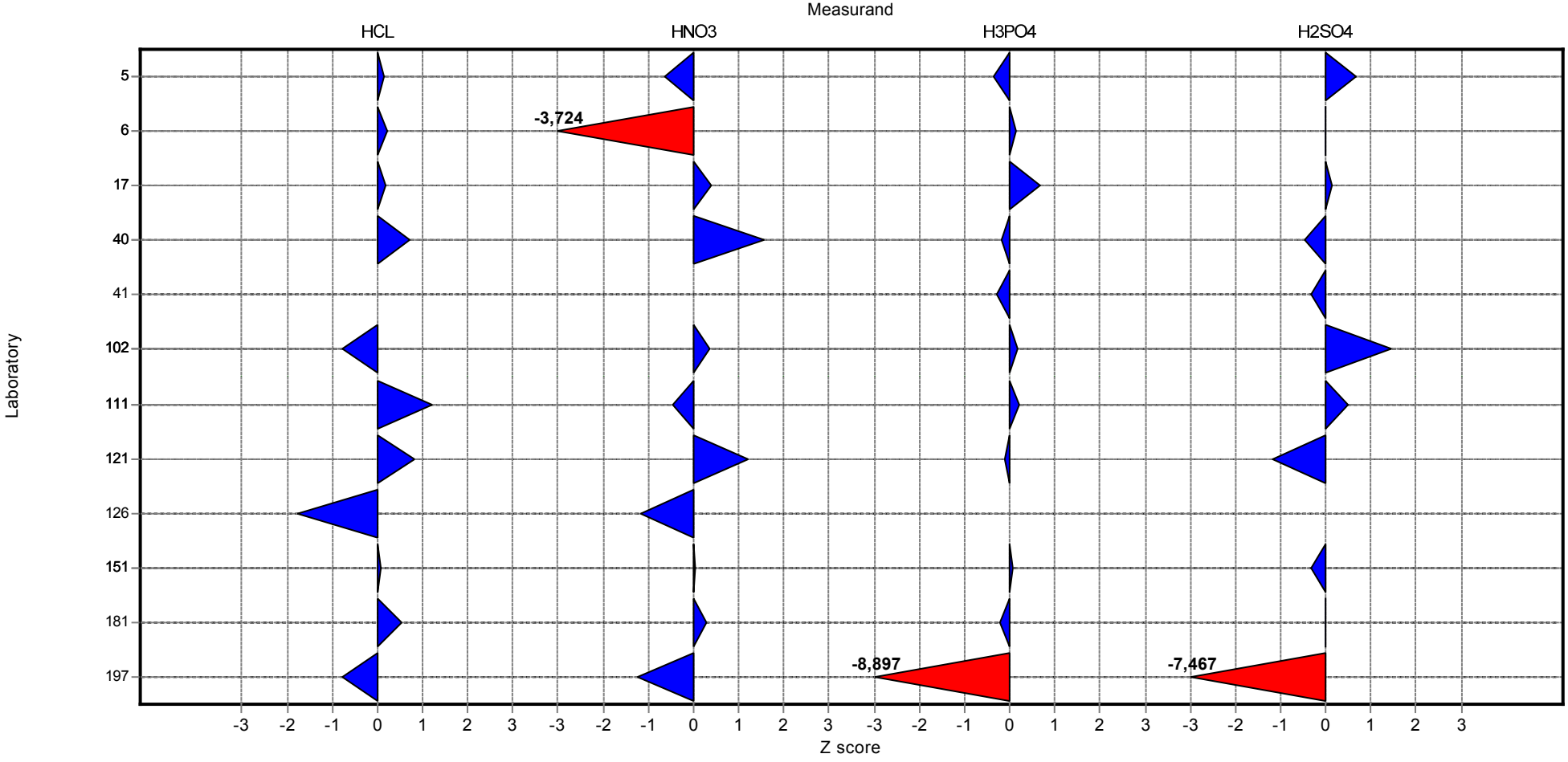
Summary results

Sample:	**sample 3**	**Mean:**	**0,060 mg/m³**
Measurand:	**sulfuric acid**	**Reproducibility s.d.:**	**0,004 mg/m³**
Method:	**ISO 5725**	**Rel. reproducibility s.d.:**	**7,03%**
No. of laboratories:	**10**	**Tolerance limits:**	**0,048 - 0,072 mg/m³ (|Z score| < 2,00)**



Sample chart of Z scores

Sample: sample 3



Questions and Answers

Participant	sample set
5	Orbo 53/Quarzfaserfilter
6	2: Orbo 53/Quarzfaserfilter
17	imprägnierter Filter
40	Filterhaltersystem Millipore mit imprägnierten Quarzglasfiltern / Proben von IFA für H2SO4 und H3PO4
41	nur SKC 226-10-03
102	3
121	Imprägnierte Quarzfilter
126	1
151	PTFE + Na2CO3 treated quartz fibre
181	imprägnierter Filter/Quarzfaserfilter
197	3

Participant	desorption solution
5	10 ml
6	Reinstw asser, Filter: 10 mL, Orbo: 5 mL
17	10 ml Eluent
40	UHQ-Wasser mit Oxalsäure als ISTD
41	10 mL einer Lösung, bestehend aus: 0,0027 M Na2CO3/L und 0,0003 M NaHCO3/L
102	demin. H2O, 20-40 mL
121	UHQ-Wasser mit Oxalsäure als ISTD
126	3,2 mmol/l Na2CO3, 1,0 mmol/l NaHCO3, 2 vol-% Aceton; 10 ml
151	w ater
181	10 ml Wasser
197	1mmol/l NaHCO3/3,2mmol/l Na2CO3 (IC-Eluent)

Participant	time of desorption	filtration	wavelength	injection volume

Ringversuch inorganic acids with sampling

Participant	time of desorption	filtration	wavelength	injection volume
5	15 min Ultraschallbad, 30 min Standzeit	ja		50
6	15 Minuten Ultraschall, 30 Minuten stehen lassen	Ja	HNO3: 210 nm	10, 20, 50, 100
17	US-Bad, 30 min	ja	-	2
40	15 Minuten im Ultraschallbad / 15 Minuten im Ultraschallbad	ja / ja	Leitfähigkeitsmessung	50 µl / 50 µl
41	15 Min. im Ultraschallbad/30 Min. Standzeit	Ja	Leitfähigkeitsmessung	50 µL
102	Ultraschall 30 Min.	ja	-	50
121	15 Minuten im Ultraschallbad / 15 Minuten im Ultraschallbad	ja / ja	Leitfähigkeitsmessung	50 µg / 50 µg
126	15 Min., US-Bad	ja	Leitf. nach chem. Suppression	20
151	2 hours	yes		25
181	15 Minuten im Ultraschallbad + 30 Minuten Wartezeit	Ja	Ionenchromatograph + Leitfähigkeitsmessung	25 µl
197	15 min U-Bad	Ja	Leitfähigkeitsdetektor	20

Participant	kind of injection	Ion Chromatographic System
5	Autosampler	Dionex DX 120
6	Autosampler	Waters: Pumpe 515, Autosampler 717, Säulenthermostat, UV-Detektor 486, Leitfähigkeitsdetektor 432
17	manuell	Metrohm 790 Personal
40	Autosampler	ICS 5000 Fa. Dionex
41	Autosampler	DIONEX IC-System DX500, Pumpe GP40, Detektor ED40
102	Autosampler	Metrohm Compact IC761 mit Autosamp. 813, LF-Detektor
121	Autosampler	ICS 5000 Fa. Dionex
126	Auto	Deut. Metrohm, IC-Detector 732, Sep-Center 733, Leitfäh.-Detektor
151	autosampler	Dionex DX500
181	Autosampler	IC: DIONEX, Typ: ICS-1600, Sampler: DIONEX-AS, Leitfähigk.
197	Autosampler	Metrohm Compact IC 761

Participant	analytical column	mobile phase
5	ION Pac AS 12A 4x200 mm	2,7 mmol Natriumcarbonat/ 0,3 mmol Natriumhydrogencarbonat
6	Waters IC-Pak Anion HR 4.6x75 mm	Borat-Gluconat-Puffer 280 µS/cm
17	Metrosep A Supp 5	1.0 mmol/l NaHCO3; 3,2 mmol NaCO3
40	Ion Pac AS 9 HC 2*250 mm Fa. Dionex	UHQ-Wasser mit KOH-Eluentengenerator
41	AG12A, Fa. DIONEX, 4x50 mm/AS12A, Fa. DIONEX, 4x200 mm	0,0027 M Na2CO3/0,0003 M NaHCO3/L
102	Metrohm Asupp5-250 - 250/4 mm	3,2 mmol/L Na2CO3, 1,0 mmol/L NaHCO3

Ringversuch inorganic acids with sampling

Participant	analytical column	mobile phase
121	Ion PAC AS 9 HC 2*250 mm Fa. Dionex	UHQ-Wasser mit KOH-Eluentengenerator
126	Metrosep A SUPP 5, 100 mm x 4 mm	3,2 mmol/l Na2CO3, 1,0 mmol/l NaHCO3, 2 vol-% Aceton; 10 ml
151	Dionex AS22	4.5mM Na2CO3 / 1.4 mM NaHCO3
181	Hauptsäule: DIONEX-AS14-4x250mm	3,5 mmol Na2CO3 und 1,0 mmol NaHCO3
197	Metrosep A Supp 5, 100 mm	1mmol/l NaHCO3/3,2mmol/l Na2CO3 (IC-Eluent)

Participant	flow rate	date of analysis	kind of pump
5	1,5	05.04.2011	Gilian 5000
6	1 mL/min	25.03.-21.04.11	GSA 4000ex
17	0,7	30.04. und 31.04.2011	PP1
40	0,36 ml/min / 0,4 ml/min	31.03.2011 / 18.04.2011	Gilian PP 5
41	1,5 mL/Min.	25.03.2011	AP Buck Inc. Type VSS 1
102	0,7 mL/Min.	28./29.03.11	PAS-Pp. GSA SG4000, Ametec Alpha 1
121	0,36 ml/min / 0,4 ml/min	31.03.2011 / 18.04.2011	Auer Escort Elf
126	0,7	29.03.11	Gilian HFS 513-A, PP5
151	1.2	13/04/2011	Gilair
181	1,05 ml/min	15.04.2011	SG10-2
197	0,7 l/min	28.4.2011	SKC

Participant	volume flow	sampling time
5	2000 ml/min	2 und 0,25
6	Filter: 2,0 L/min, Orbo: 0,5 L/min	2 h bzw . 15 min.
17	330 ml/min	60
40	ca. 1,2 L/Minute	1) 55 bis 86 Minuten 2) 56 bis 74 Minuten 3) 22 Minuten
41	250 mL/Min	Prüfgas 1-2: 60 und 120 Minuten, Prüfgas 3: 15-25 Minuten
102	ca. 2 L/Min.	Pr. 1+2 je 60 Min./Pr. 3 - 15 Min.
121	1 - 1,1 l/min	Prüfgas 1: 62 bis 90 min, Prüfgas 2: 60 bis 91 min, Prüfgas 3: 16 min
126	1.: 0,46, 0,48; 2.: 0,53, 0,46; 3.: 0,58, 0,66 l/Min.	1: 1,08; 2.: 1,03; 3.: 0,25
151	1 litre/min	0.2 - 1
181	2,00 l/min	2,0 Stunden bzw . 15 Minuten
197	ca. 2 l/min	Probe 1: 2h; Probe 2: 1h; Probe 3: 15min

Ringversuch inorganic acids with sampling

Participant	volume flow measurement
5	Fa. SKC DryCal
6	Gilian Gilibrator-2
17	DigiCal
40	DryCal der Fa. Analyt
41	digitaler Massendurchflussmesser FA. Analyt
102	Buck-Calibrator
121	DryCal - Bios International
126	BIOS Drycal, Defender 510-M
151	TSI flow meter
181	DryCal
197	Gilibrator