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Geschäftsführer: Ralf Klaus Blecher // Amtsgericht Göttingen HRB 130263
www.crb-gmbh.de // labor@crb-gmbh.de

Analyse Service GmbH

RFA Ringversuch SISECAM Glas- und Sandproben - Glas 2

Veranstalter des Ringversuchs:	SISECAM, Türkei
Ringversuchsmaterial:	Glass Sample 2
RV geschlossen:	2018 – 2
Literatur:	Round Robin Inter Laboratories Comparison Proficiency Test Report Glass and Sand Samples

Hauptelemente [MA%]

	CRB	RV	1sRV	Z-Score
SiO_2	71,800	71,913	0,388	-0,290
Al_2O_3	1,590	1,503	0,038	2,290
Fe_2O_3tot	0,023	0,020	0,003	1,310
TiO_2	0,039	0,042	0,003	-0,930
CaO	8,340	8,347	0,118	-0,060
MgO	3,460	3,450	0,031	0,320
Na_2O	14,190	14,405	0,477	-0,450
K_2O	0,050	0,059	0,013	-0,650
SO_3	0,170	0,222	0,062	-0,850

Legende

CRB: Ergebnisse CRB – **RV:** Ergebnisse Ringversuch -- **1s-RV:** Standardabweichung Ringversuch
Z-Score: Differenz des Messwertes vom Mittelwert des Ringversuchs -- ***** Wert nicht zertifiziert

Round Robin
Inter Laboratories Comparison
Proficiency Test Report

Glass and Sand Samples

Yenişehir-Bursa, 14.01.2018

Statistics-Report-Coordinator of PT
Mehmet Ali AK
Lead Researcher

Form No: KG.FO.20-8	**Yayın Tarihi:** 08.01.2007	**Revizyon No:** 03	**Revizyon Tarihi:** 06.06.2017

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1. INTRODUCTION

Chemical analysis of glasses and sands are used for process control in glass manufacture, for demonstration specification compliance and for relating chemical properties to performance attributes. X-ray fluorescence analysis is a widely used technique for the analysis of oxidic materials. This report is an Interlaboratory study on chemical analyses of glass and sand samples by X-ray fluorescence analysis. In this interlaboratory study 10 laboratories did register for participation. 9 laboratories provided results for glass samples covering 9 analytes, SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, Na_2O, K_2O, SO_3. And 10 laboratories provided results for sand samples covering 8 analytes, SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, Na_2O, K_2O. All evaluations are performed in agreement with ISO 13528:2015 Statistical methods for use in proficiency testing by interlaboratory comparison.

Interlaboratories Comparison Test Provider

Turkiye Sise ve Cam Fabrikalari AS - Yenisehir Regional Laboratory

Trakya Yenisehir Cam Sanayi, YOSAB Tabakhane Mah, Sisecam Cad, No:2

Yenisehir-Bursa/TURKEY

Coordinator and Responsible for evaluation and data processing: Mehmet Ali AK

2. PARTICIPANTS

2.1. Participant Accreditation

It is important to know whether or not the participant laboratory works under “ISO/IEC 17025:2017 General requirements for the competence of testing and calibration laboratories” accreditation. Therefore, we asked this information to all laboratories who were participated. In this study, all laboratories work under ISO/IEC 17025 accreditation.

2.2. Number of Participants

In this interlaboratory study 10 laboratories did register for participation. 9 laboratories provided results for glass samples covering 9 analytes, SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, Na_2O, K_2O, SO_3. And 10 laboratories provided results for sand samples covering 8 analytes, SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, Na_2O, K_2O.

2.3. Participants Contact Information

	Laboratory	Contact Person	Telephone	E-Mail
1	Şişecam Yenişehir Bölge Laboratuvarı (Turkey)	Mehmet Ali Ak	90 850 206 13 68	meak@sisecam.com
2	Şişecam Malzeme Analiz ve Karakterizasyon Müdürlüğü (Turkey)	Erdem Yıldırım	90 850 206 55 77	eyildirim@sisecam.com
3	Glass Technology Services (UK)	Heather Marsh	+44 (0) 114 290 1850	h.marsh@glass-ts.com
4	Esan Eczacıbaşı Laboratuvarı (Turkey)	Y. Ogün Beydoğan	90 216 581 64 00	yasin.beydogan@eczacibasi.com.tr
5	Zentrum für Glas- und Umweltanalytik GmbH (Germany)	Norbert Schulze	+49 (0) 3677-8452-23	N.Schulze@zgu.de
6	Tübitak BUTAL (Turkey)	M. Akif Çimenoğlu	90 224 233 94 40	akif.cimenoglu@tubitak.gov.tr
7	Dorfner Anzaplan Analysenzentrum und Anlagenplanungsgesellschaft mbH (Germany)	Thomas Bach	+49 962 282-185	thomas.bach@dorfner.com
8	Çanakkale Seramik (Turkey)	Yıldız Yıldırım	90 286 416 17 17	yildizyildirim@kale.com.tr
9	Terrachem GmbH (Germany)	Daniel Auwärter	+49 (0) 621 87 67 97 15	daniel.auwaerter@terrachem.de
10	CRB Analyse Service GmbH (Germany)	Stefan Pierdzig	+49 (0) 5505 // 940 98-13	pierdzig@crb-gmbh.de

3.SAMPLES

3.1. Sample Selection

Interlaboratories Comparison Test Items

Test item	Description
Glass Sample 1	1-Float Glass (high Fe_2O_3)
Glass Sample 2	2-Tableware Glass (low Fe_2O_3)
Sand Sample 1	1-Sand Sample (high Fe_2O_3)
Sand Sample 2	2-Sand Sample (low Fe_2O_3)

3.2. Sample Preparation

30 pieces of flat glass were provided by Yenisehir Regional Laboratory. 30 pieces of tableware products, 20 kilograms of high Fe_2O_3 sand and 20 kilograms of low Fe_2O_3 sand were provided by Eskisehir Regional Laboratory. Sand samples were dried at 110°C for 3 hours. The drying process must result in a constant weight. After cooling, the samples were subjected to reduction by quartering. Each sand sample was divided to three (3) bags. Each sample in bags was grinded in a grinder machine.

3.3. Sample Homogeneity and Stability Testing

The measurements for the homogeneity and stability studies were performed by Yenisehir Regional Laboratory. Homogeneity and stability were evaluated according to "ISO 13528:2015 Statistical methods for use in proficiency testing by interlaboratory comparison" . For each glass sample, 5 (five) glass pieces were randomly selected and measured. For each sand sample, samples were divided to 3 (three) bags. And from each bag 5 (five) samples were randomly selected and measured. The data showed that the samples were homogenous.

3.4. Sample Distribution

The samples were dispatched on 11th October 2017. Each participant received two (2) labeled glass samples and two (2) labeled brown bottles including sand samples. The closing date for submitting results was the 20th November 2017, which was further extended to 15th December 2017 for some laboratories that encountered problems with sample delivery and results.

4. EXPERIMENTAL METHOD:

Recommendation for sand samples

Sand samples are moisture sensitive. It has to be dried for minimum 1 hour at 110^{o}C prior use. The drying process must result in a constant weight. 1 g of the dried sample is mixed with 4 g of flux in a platinum/gold (%95:5) crucible and melted in an automatic fusion machine or melted manually in a muffle furnace.

Recommendation for glass samples

Glass samples are stable materials. For sample preparation grinding and polishing are adviced for more intensity in XRF machine, also for more stable and accurate results.

However, since each laboratory has its own sample preparation method, there is no requirement in this regard.

5. STATISTICAL EVALUATION OF PT:

Calculation of Mean m

The mean m for all laboratories is calculated using the Hampel estimator (ISO/TS 20612:2007 9.2.3) based on the laboratory means μ.

Calculation of reproducibility standard deviation s_R

The reproducibility standard deviation s_R is calculated using the Q-method (ISO/TS 20612:2007 9.2.3).

Calculation of repeatability standard deviation s_r

The repeatability standard deviation s_r is also calculated using the Q-method.

Uncertainty of Mean U

The uncertainty of mean U for k=2 (95% confidence level) is calculated from the reproducibility standard deviation s_R and the laboratories p with valid data according ISO 13528:2015:

$$U = 2 * 1.25 * \frac{s_R}{\sqrt{p}} \quad (1)$$

Laboratory performance

Laboratory proficiency assessment is based on z-scores.

From all laboratory means μ, the z-score z is calculated:

$$z = \frac{m-\mu}{s_R} \quad (2)$$

m	Mean value of all laboratories (assigned value)
μ	Mean value of individual laboratory
sR	Reproducibility standard deviation

Assessment of z-scores

$\|z\| <= 2.0$	indicates, satisfactory' performance = generates no signal
$2.0 < \|z\| < 3.0$	indicates, questionable' performance = generates a warning signal
$\|z\| >= 3.0$	indicates, unsatisfactory' performance = generates an action signal

All laboratory means μ with $3 >= |z| >= 2$ were highlighted with a yellow color, z-scores with $|z| >= 3$ were highlighted with a red color.

Note: Non numerical results (e.g. < % x) were not evaluated.

6. RESULTS

For all samples and measurands, 312 data was collected in total. The data was calculated according to "ISO 13528:2015 Statistical methods for use in proficiency testing by interlaboratory comparisons". 36 data was calculated as outliers. It was seen that 89% of the data was successful.

6.1. Summary Results of Glass Sample - 1

Table 1: Glass Sample – 1 Measurand SiO_2

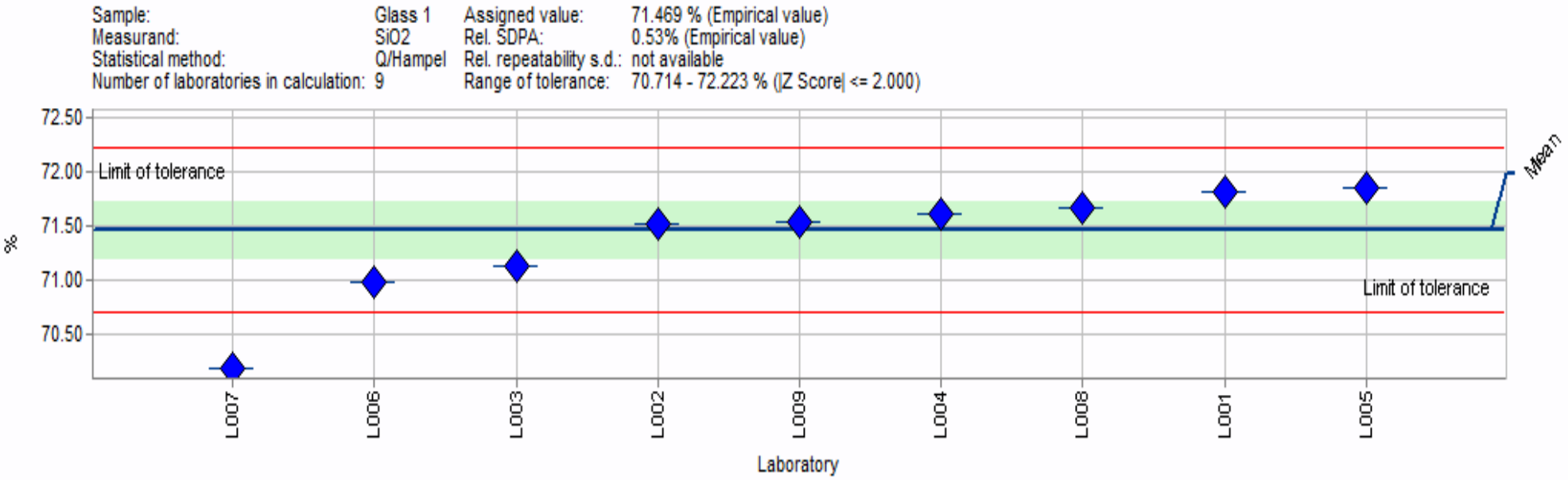


Table 2: Glass Sample – 1 Measurand Al_2O_3

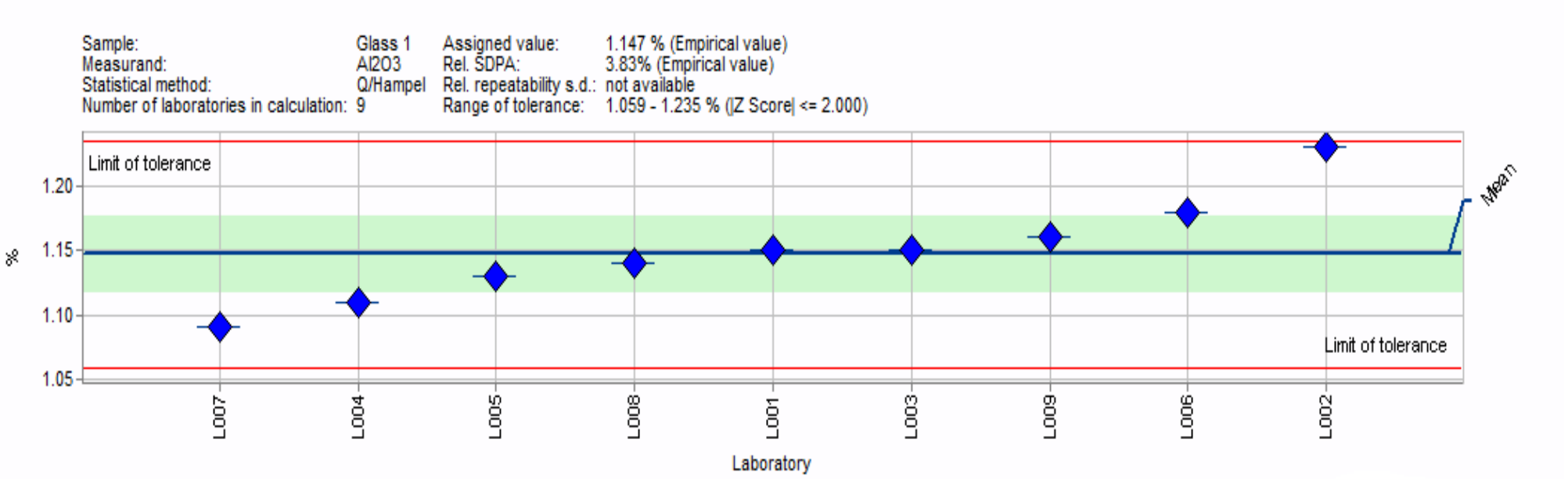


Table 3: Glass Sample – 1 Measurand Fe_2O_3

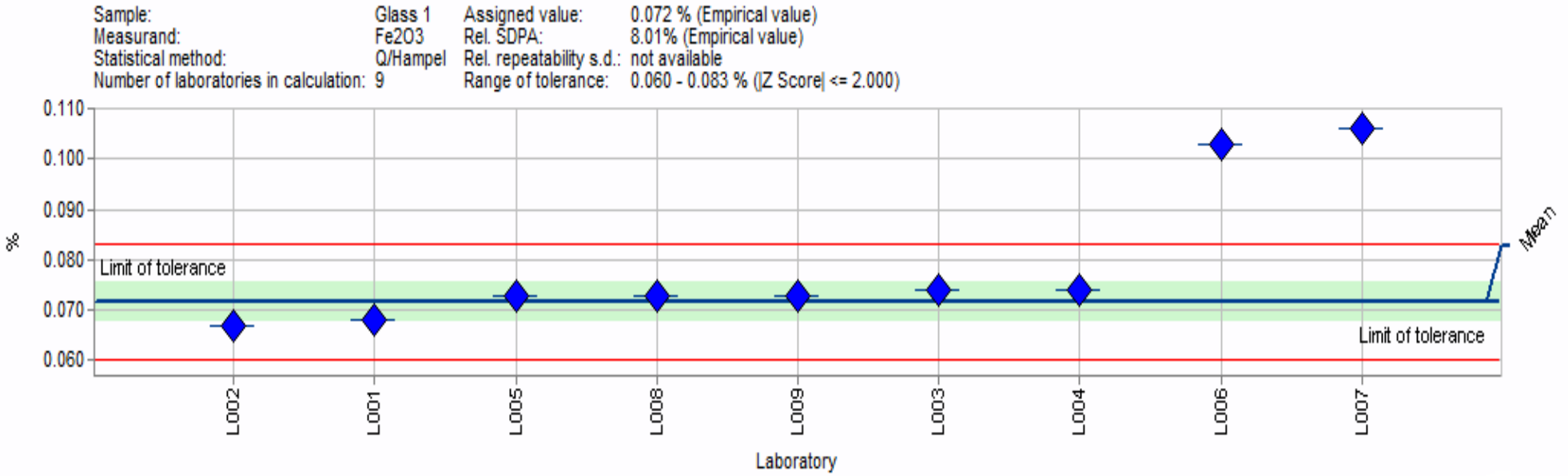


Table 4: Glass Sample – 1 Measurand TiO_2

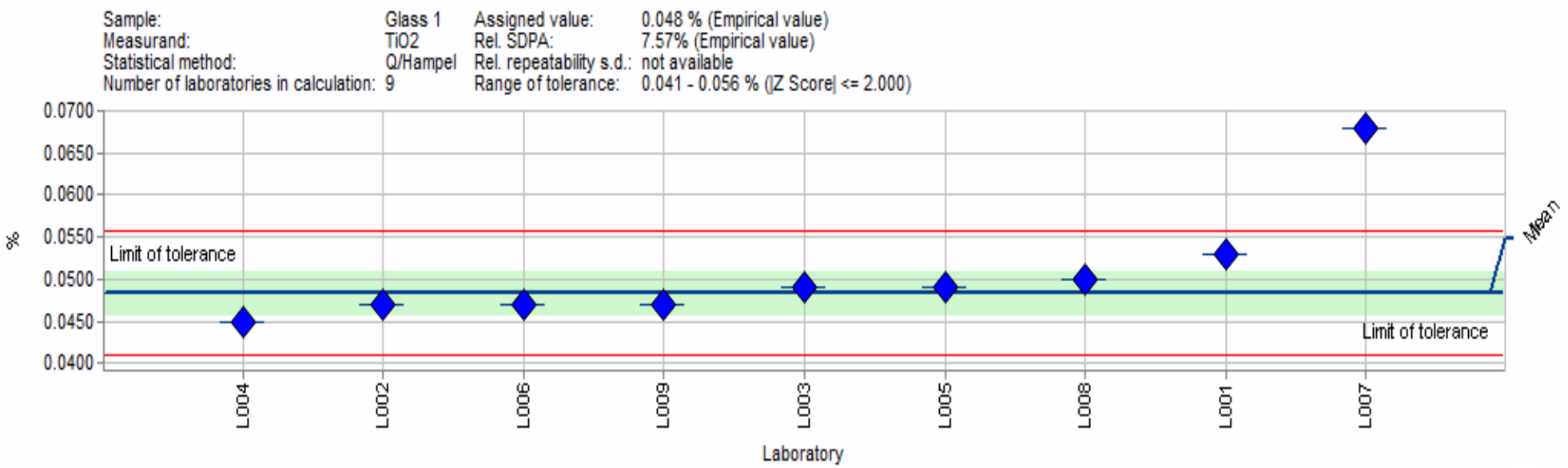


Table 5: Glass Sample – 1 Measurand CaO

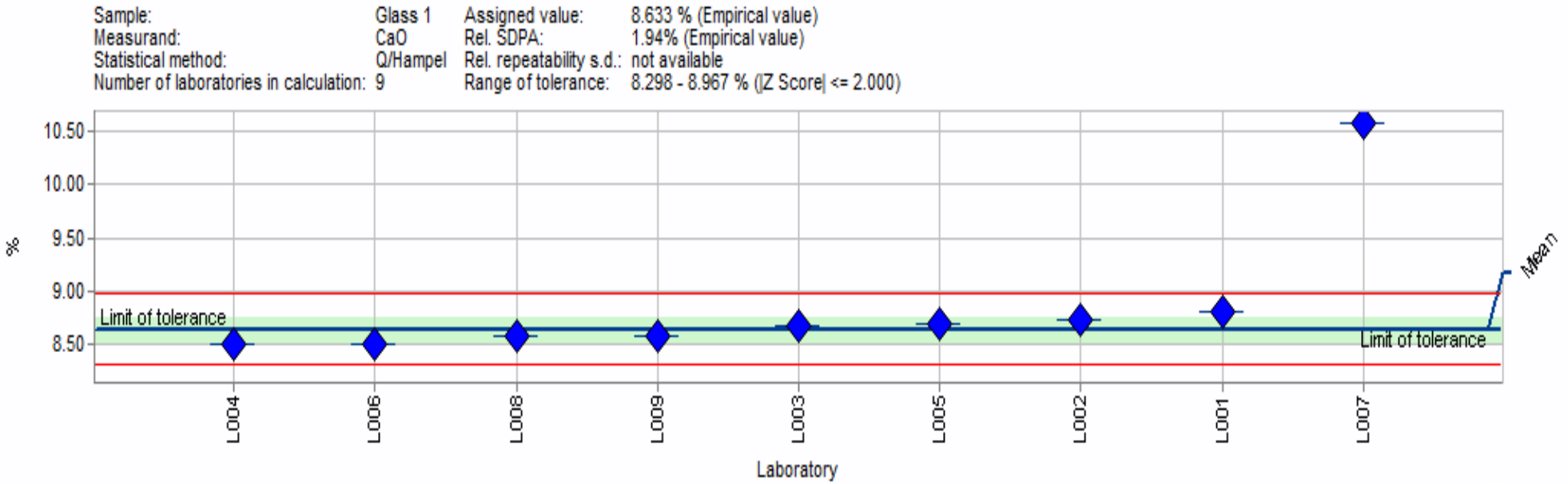


Table 6: Glass Sample – 1 Measurand MgO

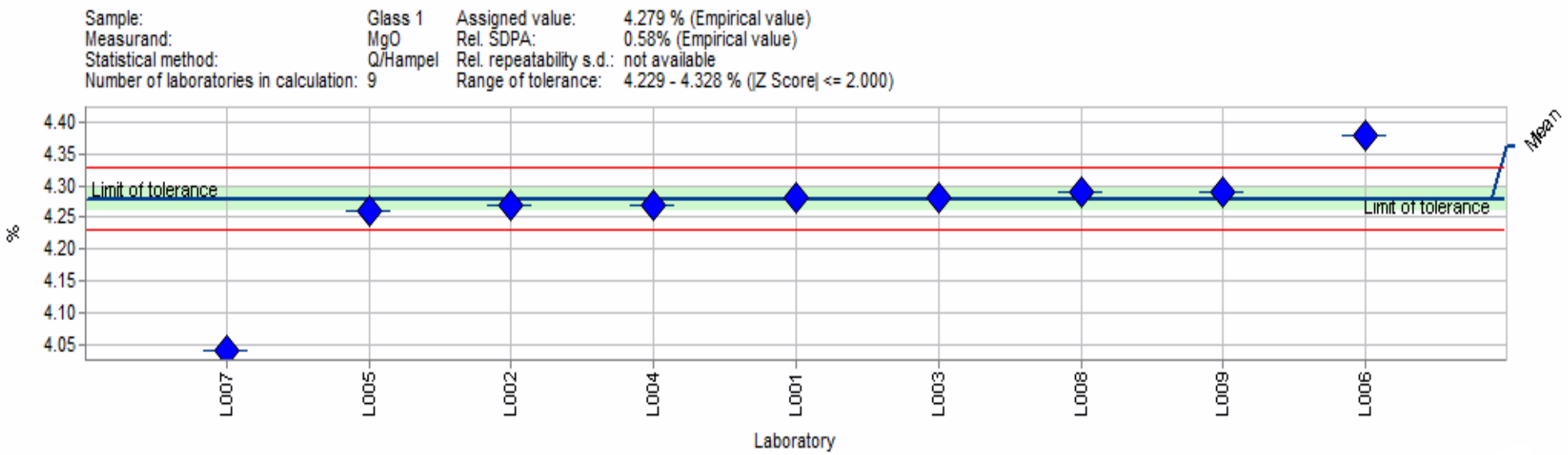


Table 7: Glass Sample – 1 Measurand Na_2O

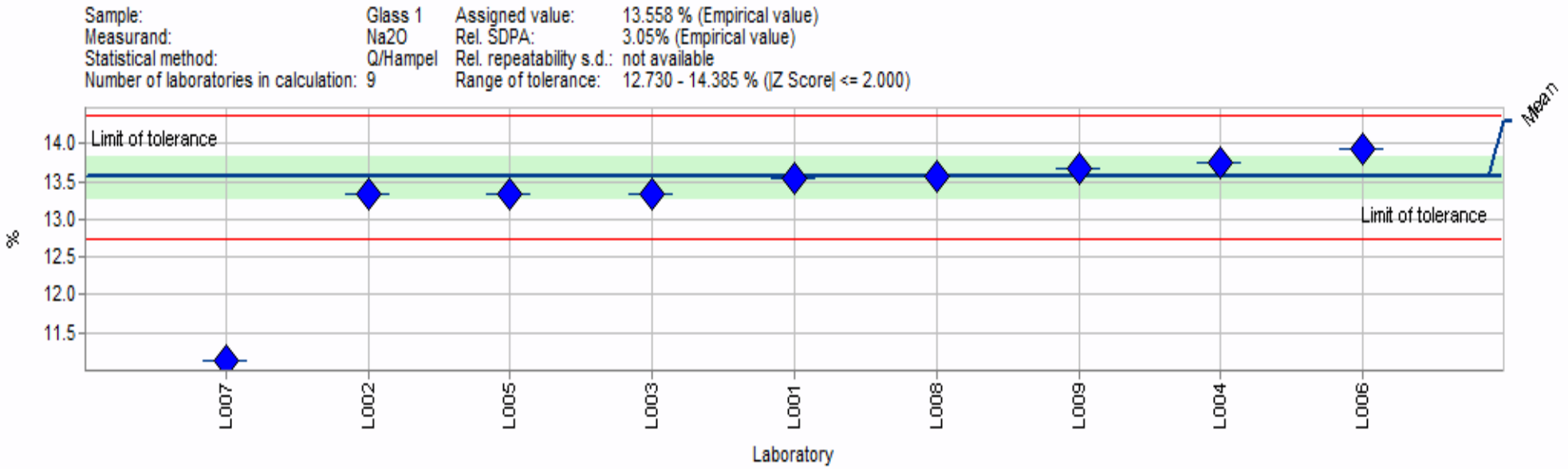


Table 8: Glass Sample – 1 Measurand K_2O

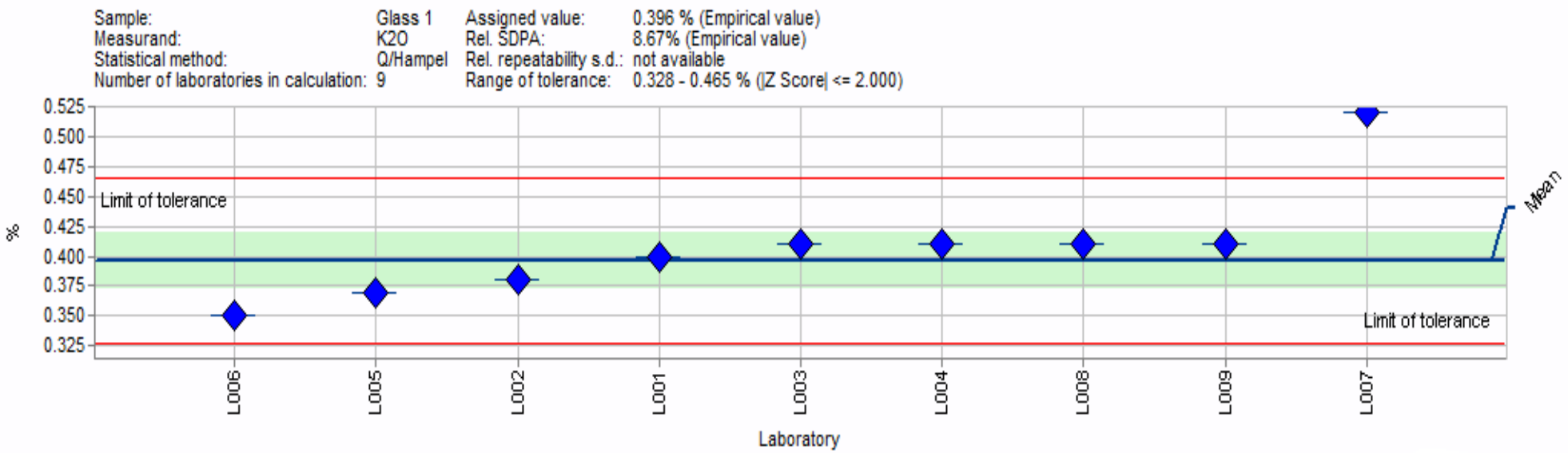
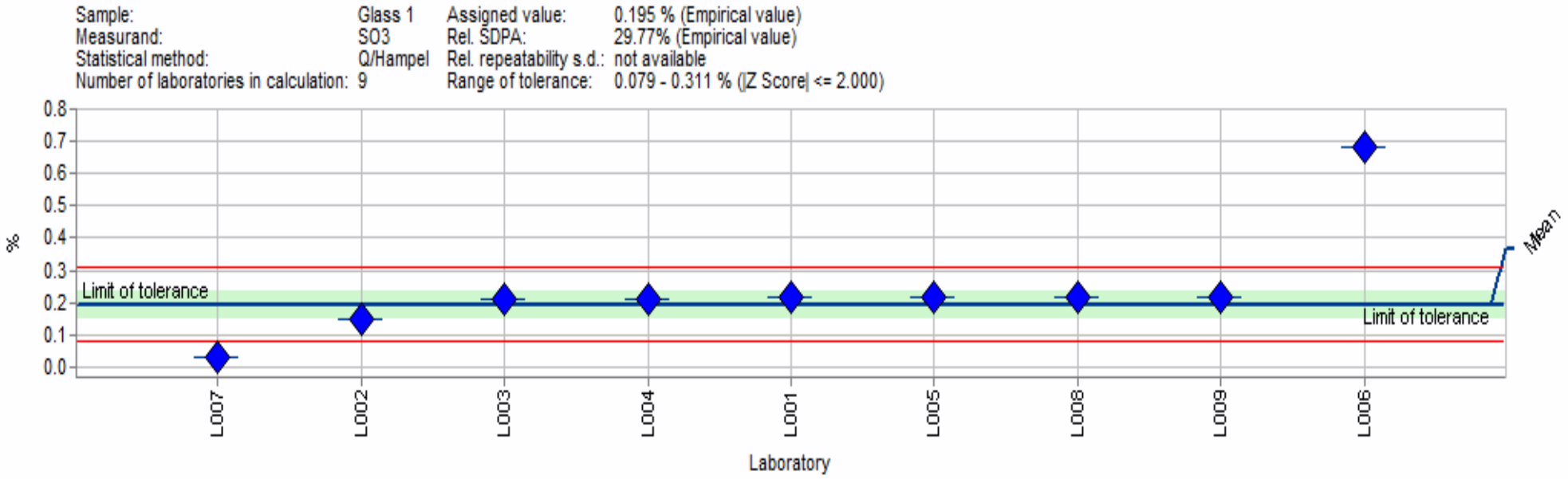


Table 9: Glass Sample – 1 Measurand SO_3



6.2. Summary Results Of Glass Sample - 2

Table 10: Glass Sample – 2 Measurand SiO_2

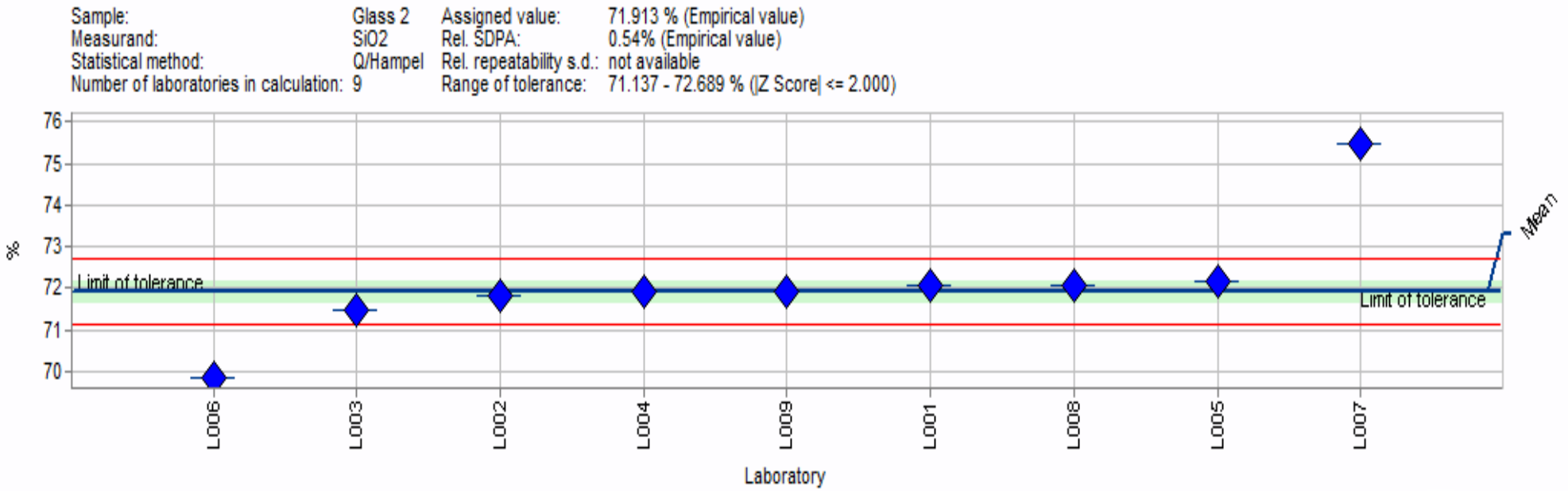


Table 11: Glass Sample – 2 Measurand Al_2O_3

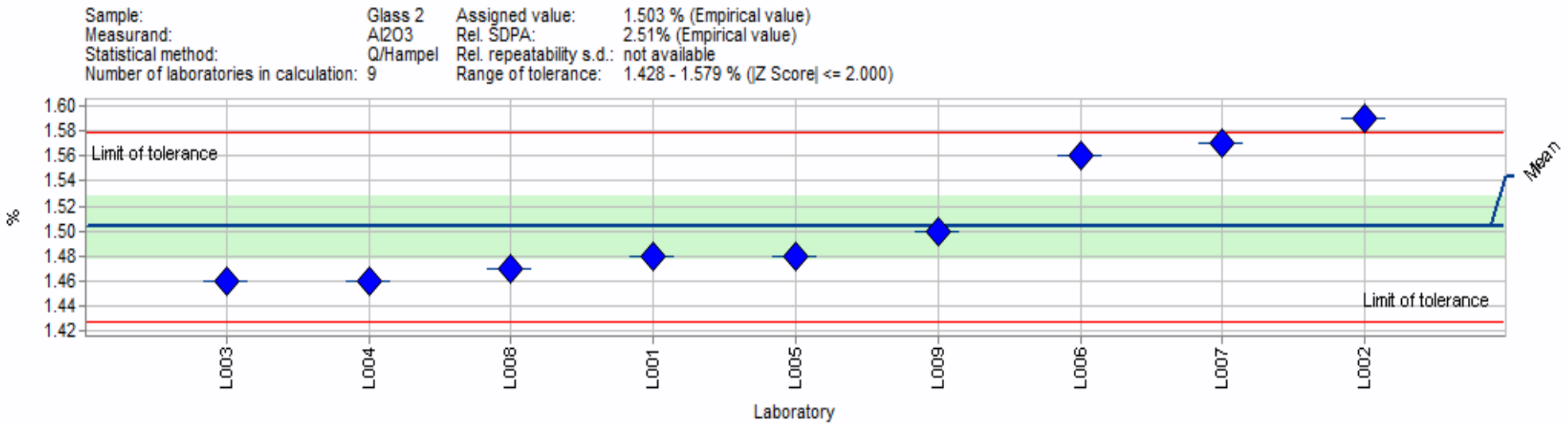


Table 12: Glass Sample – 2 Measurand Fe_2O_3

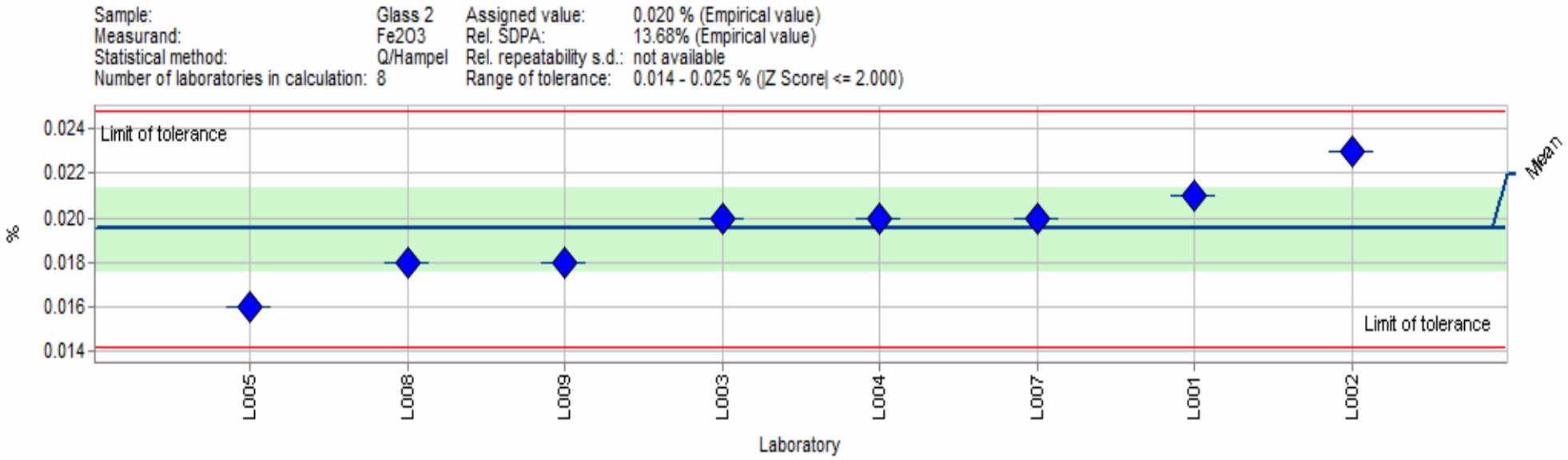


Table 13: Glass Sample – 2 Measurand TiO_2

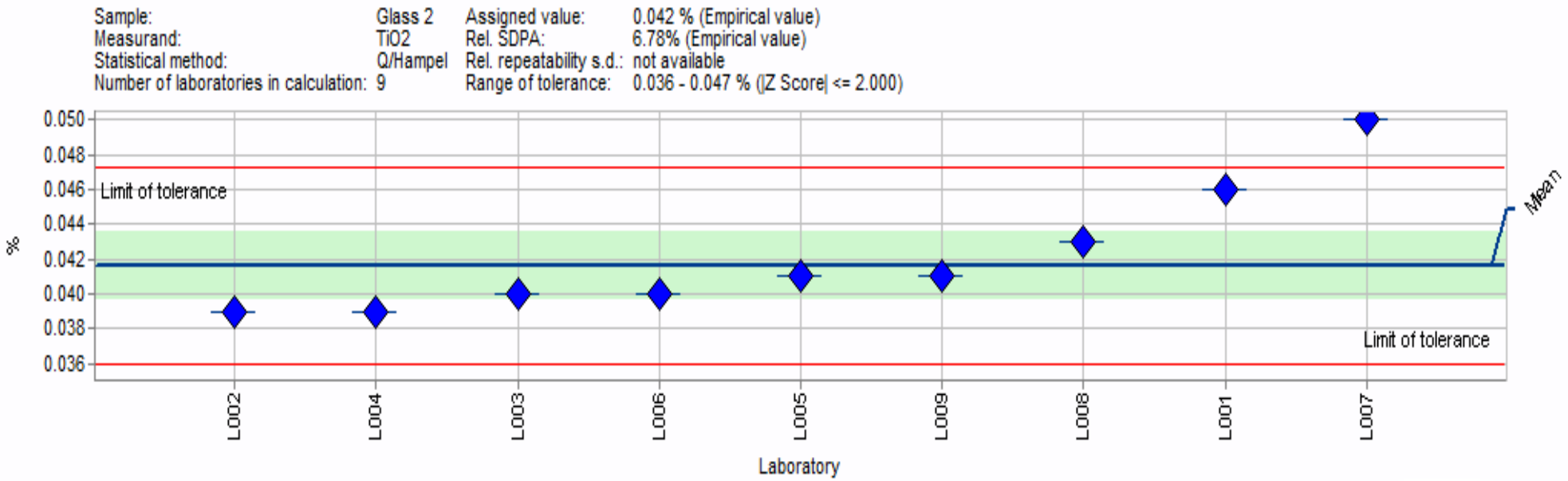


Table 14: Glass Sample – 2 Measurand CaO

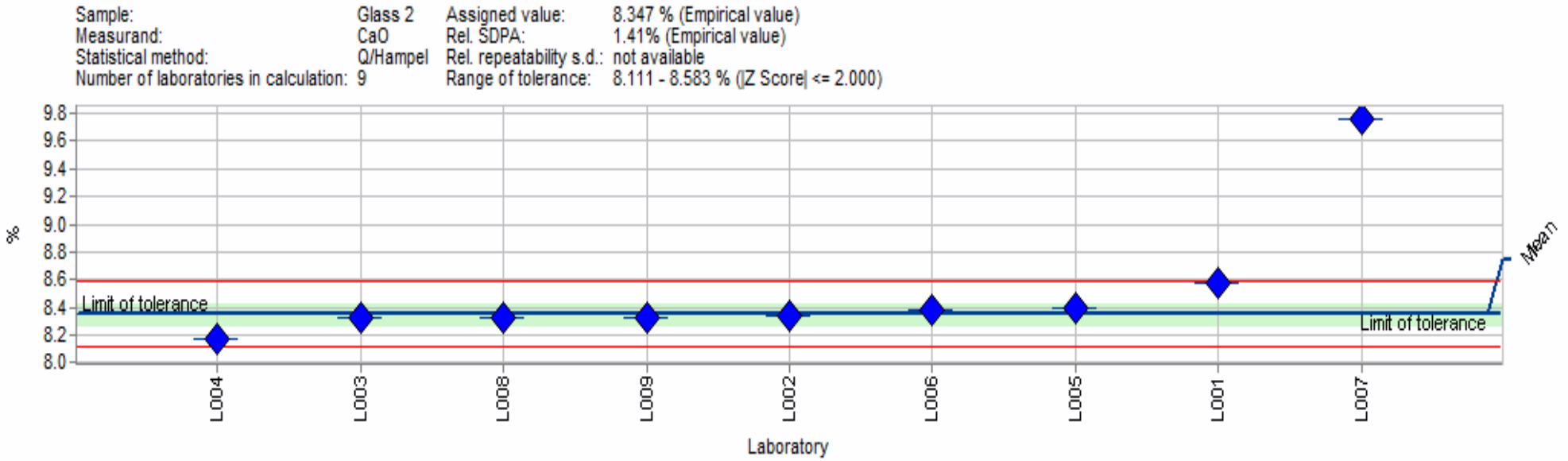


Table 15: Glass Sample – 2 Measurand MgO

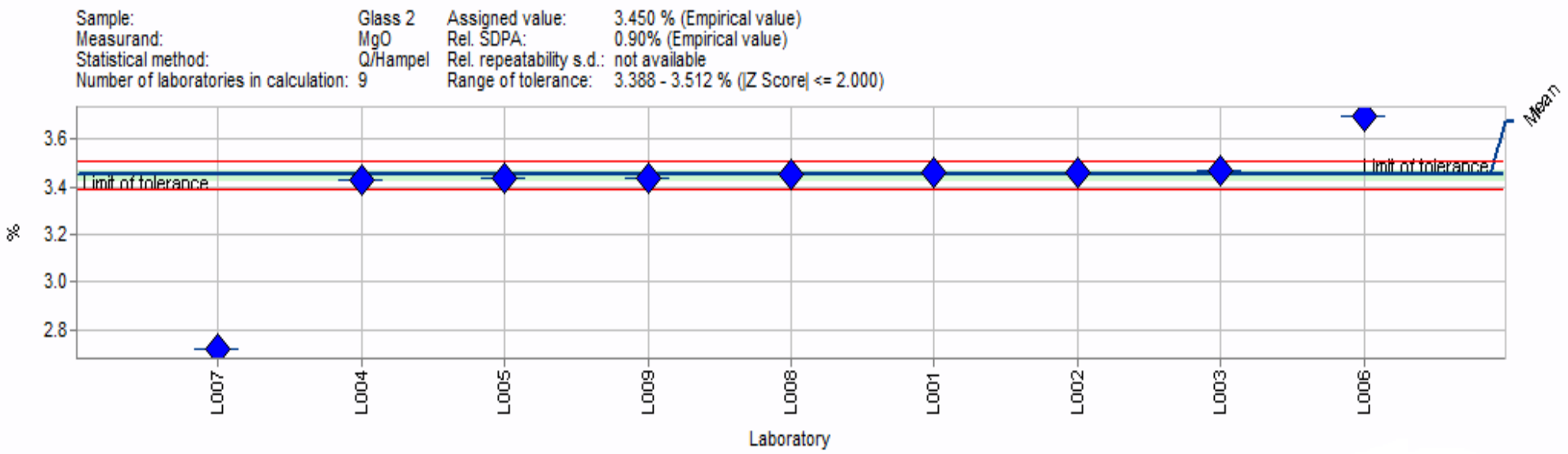


Table 16: Glass Sample – 2 Measurand Na_2O

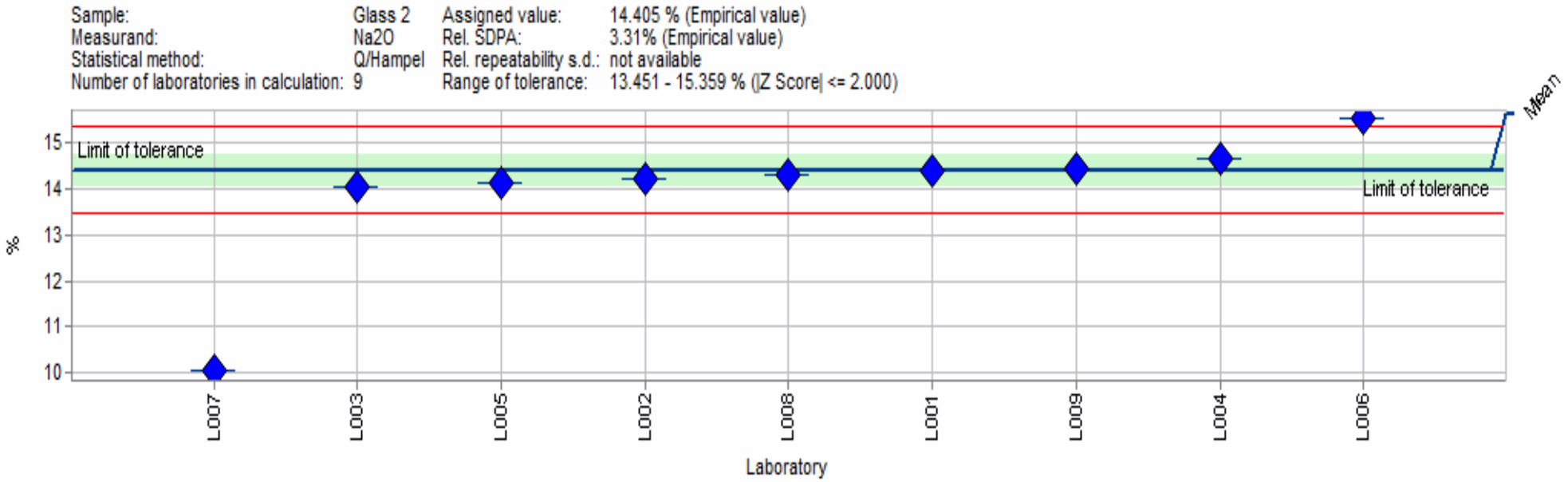


Table 17: Glass Sample – 2 Measurand K_2O

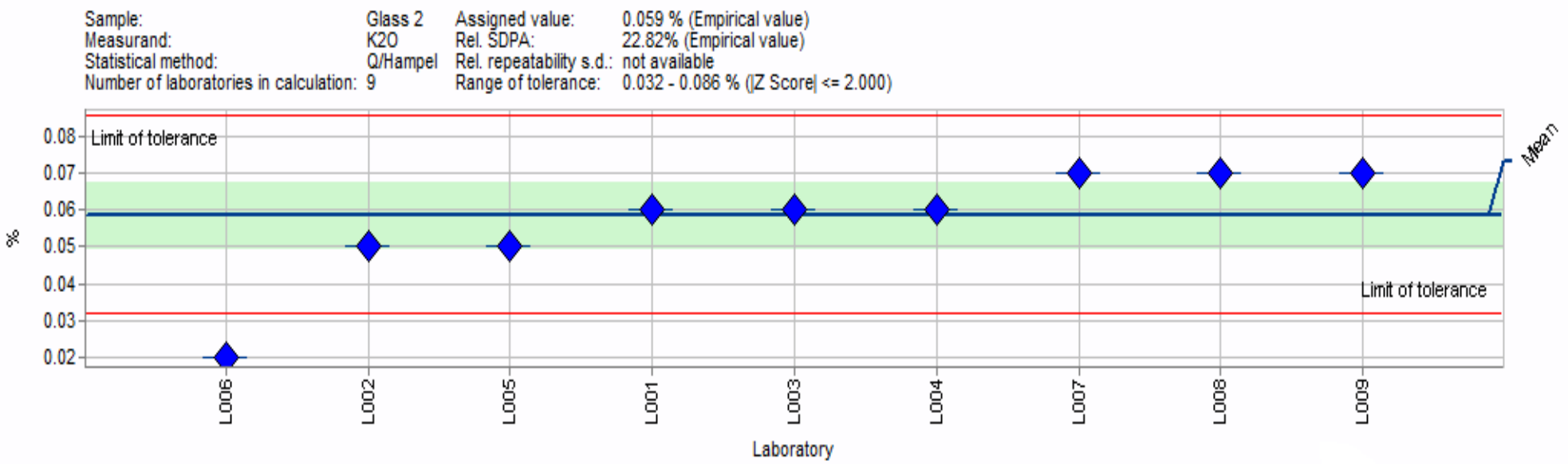
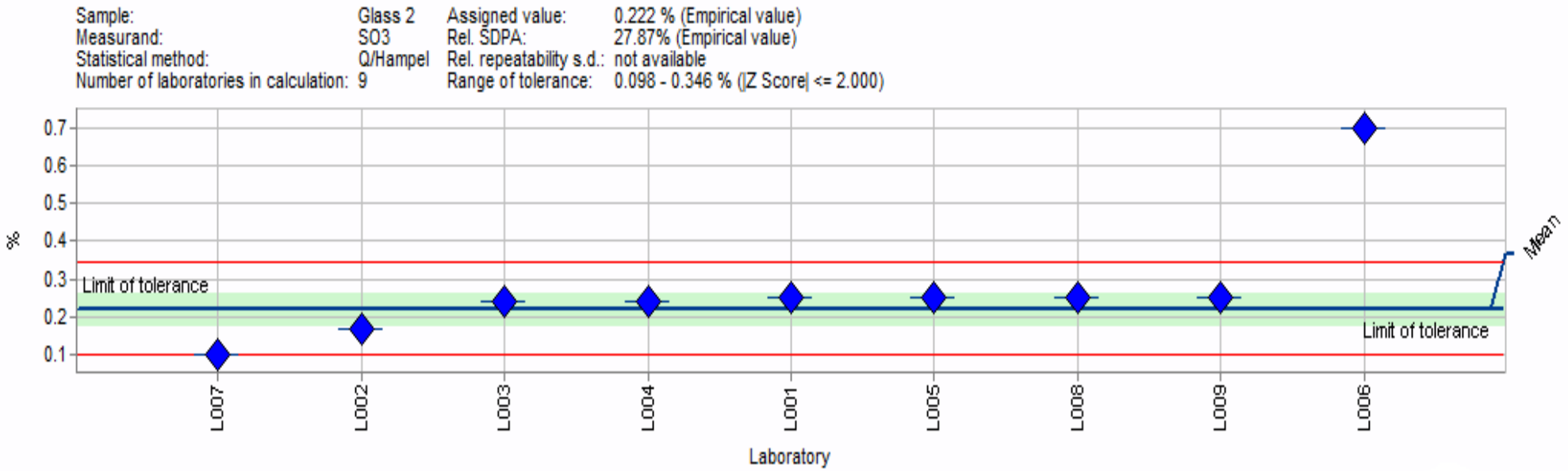


Table 18: Glass Sample – 2 Measurand SO_3



6.3. Summary Results Of Sand Sample - 1

Table 19: Sand Sample – 1 Measurand SiO_2

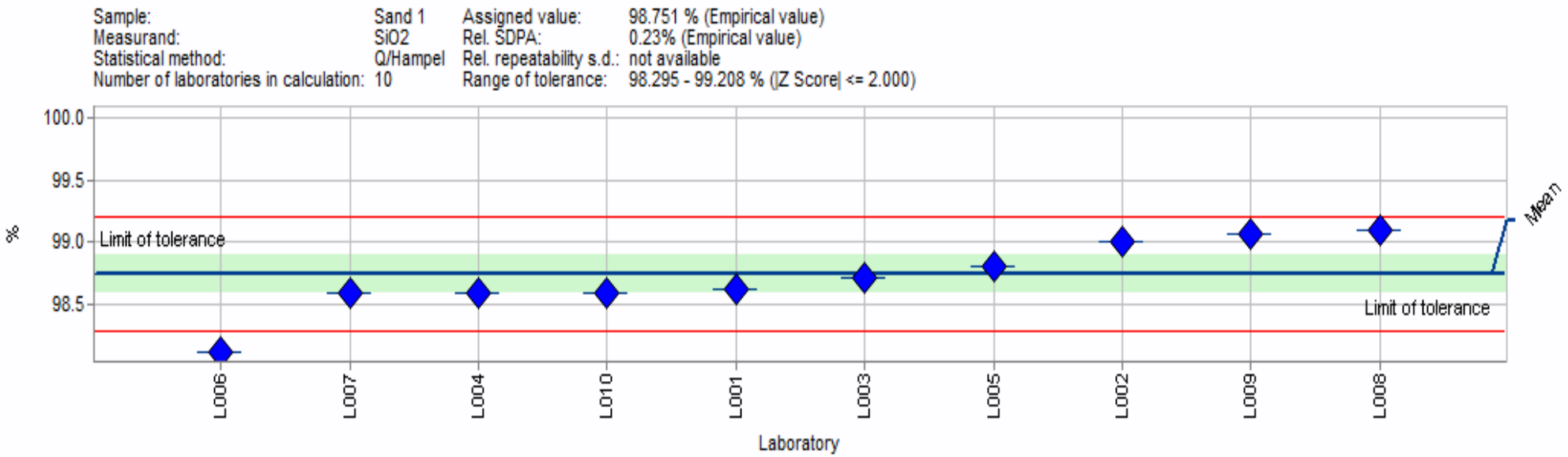


Table 20: Sand Sample – 1 Measurand Al_2O_3

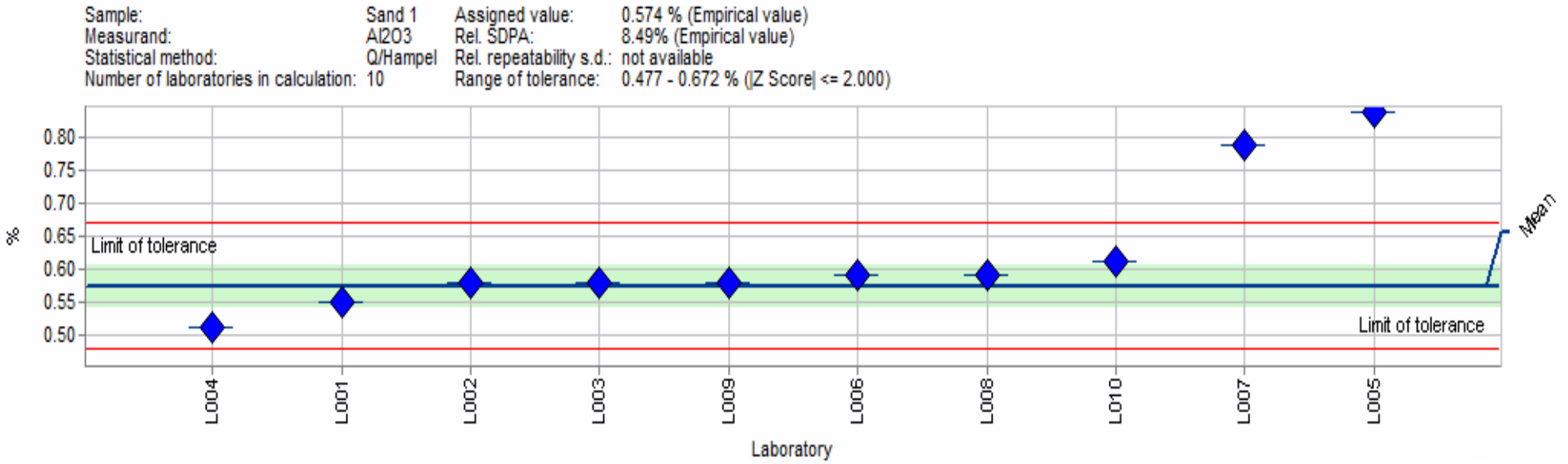


Table 21: Sand Sample – 1 Measurand Fe_2O_3

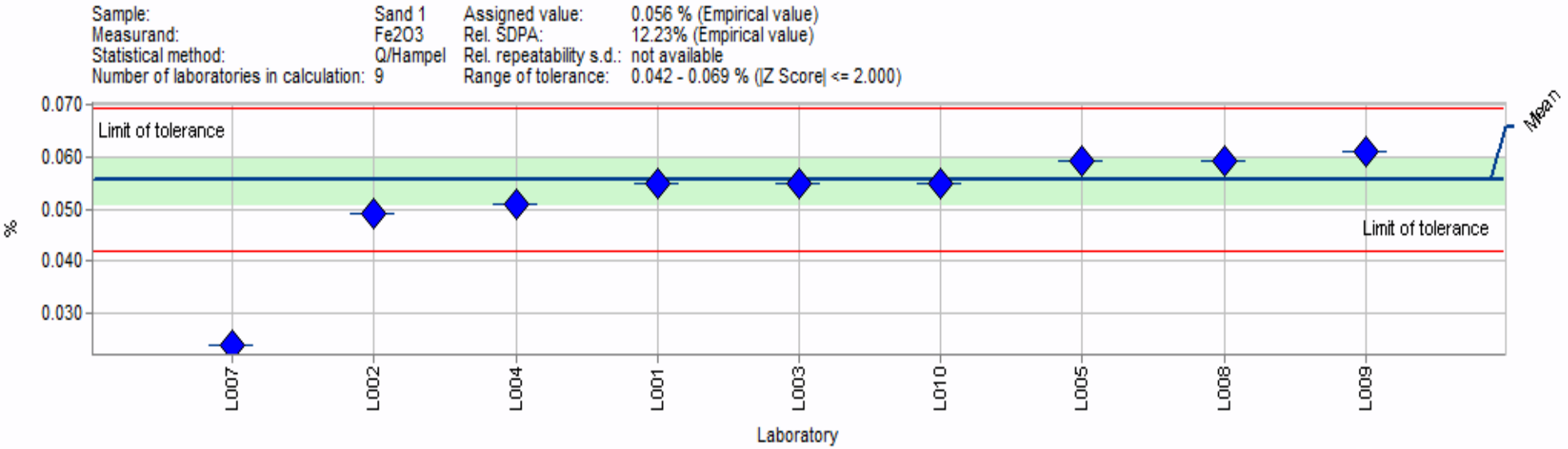


Table 22: Sand Sample – 1 Measurand TiO_2

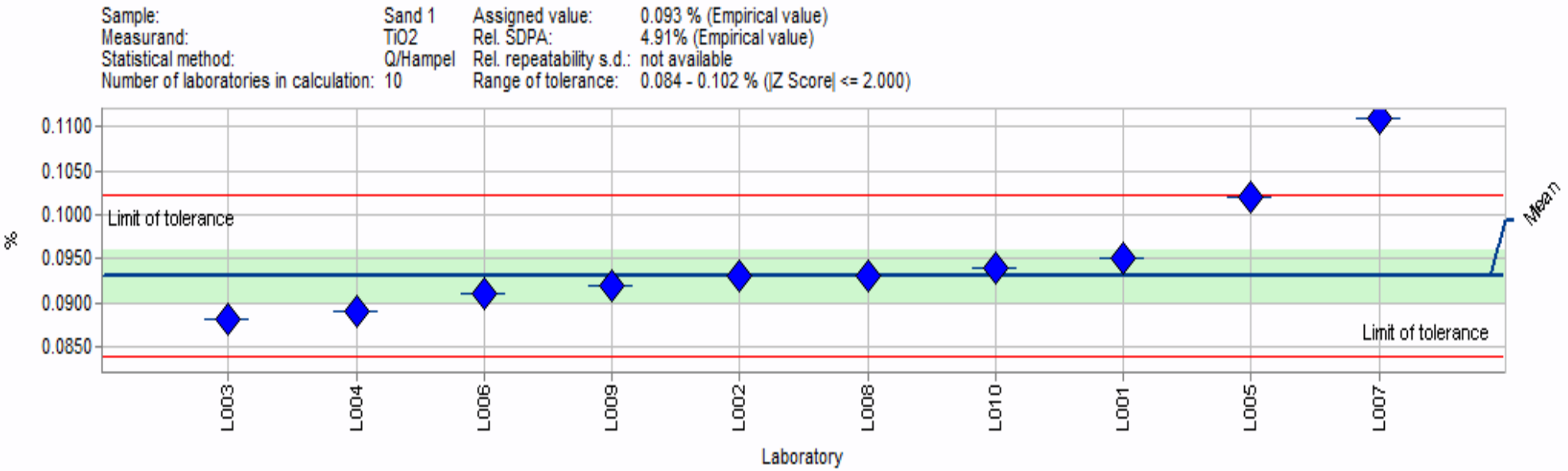


Table 23: Sand Sample – 1 Measurand CaO

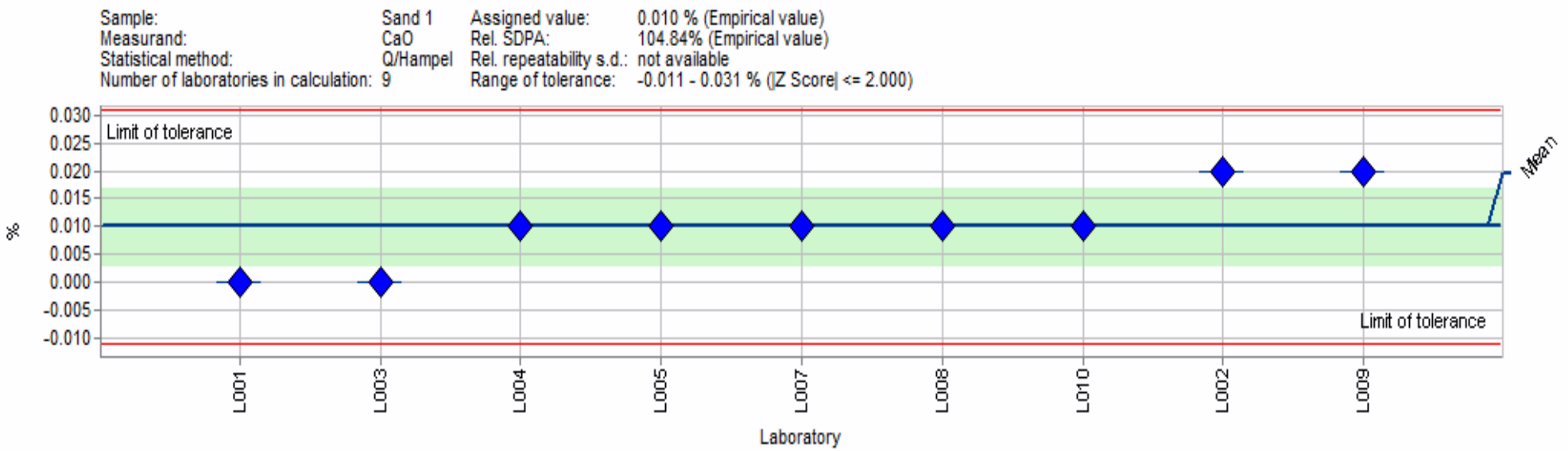


Table 24: Sand Sample – 1 Measurand MgO

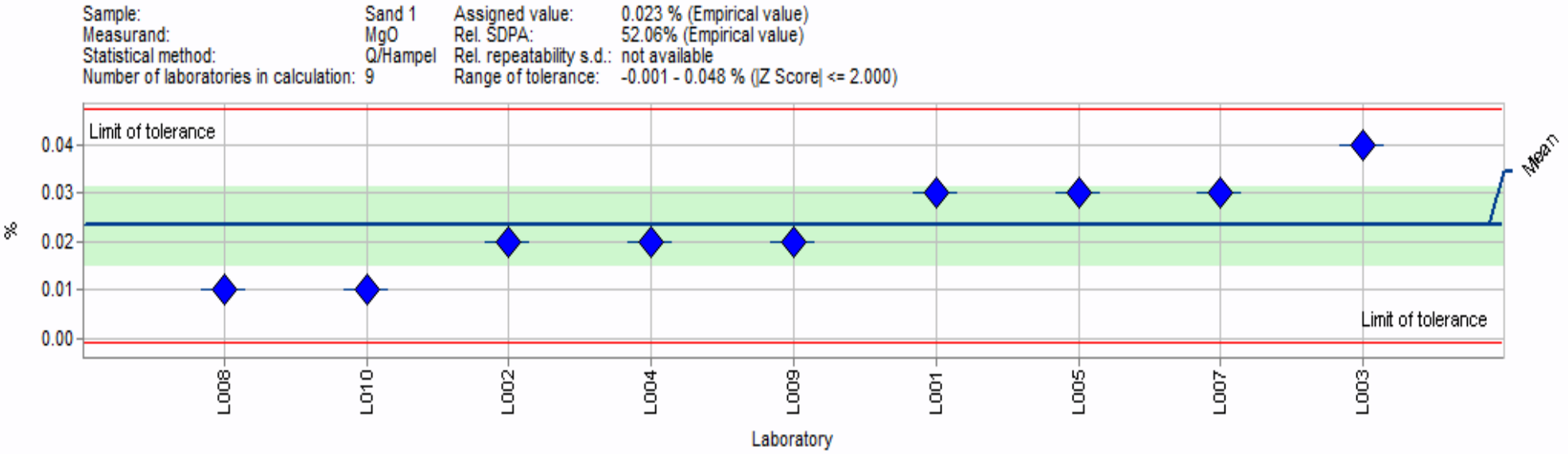


Table 25: Sand Sample – 1 Measurand Na_2O

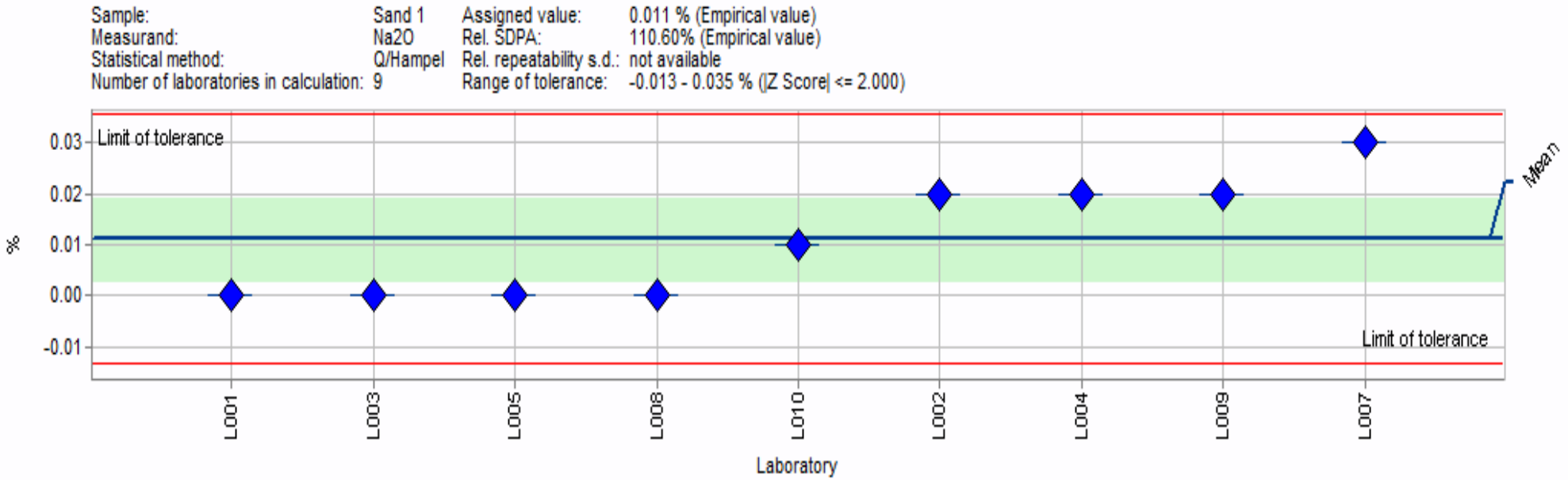
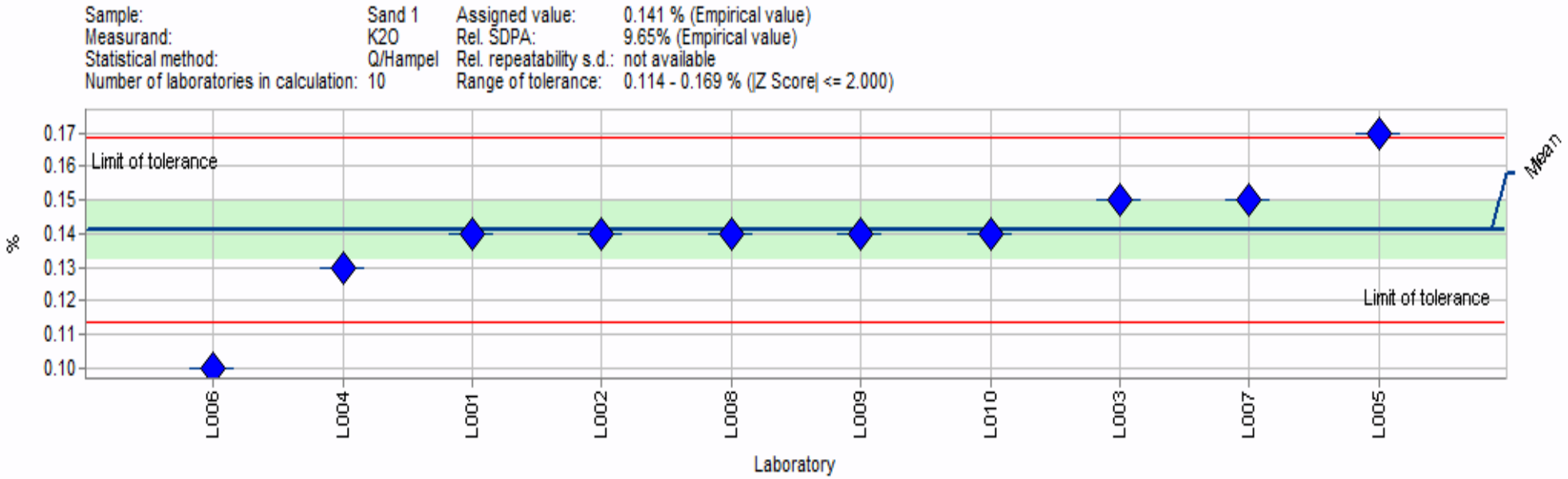


Table 26: Sand Sample – 1 Measurand K_2O



6.4. Summary Results Of Sand Sample - 2

Table 27: Sand Sample – 2 Measurand SiO_2

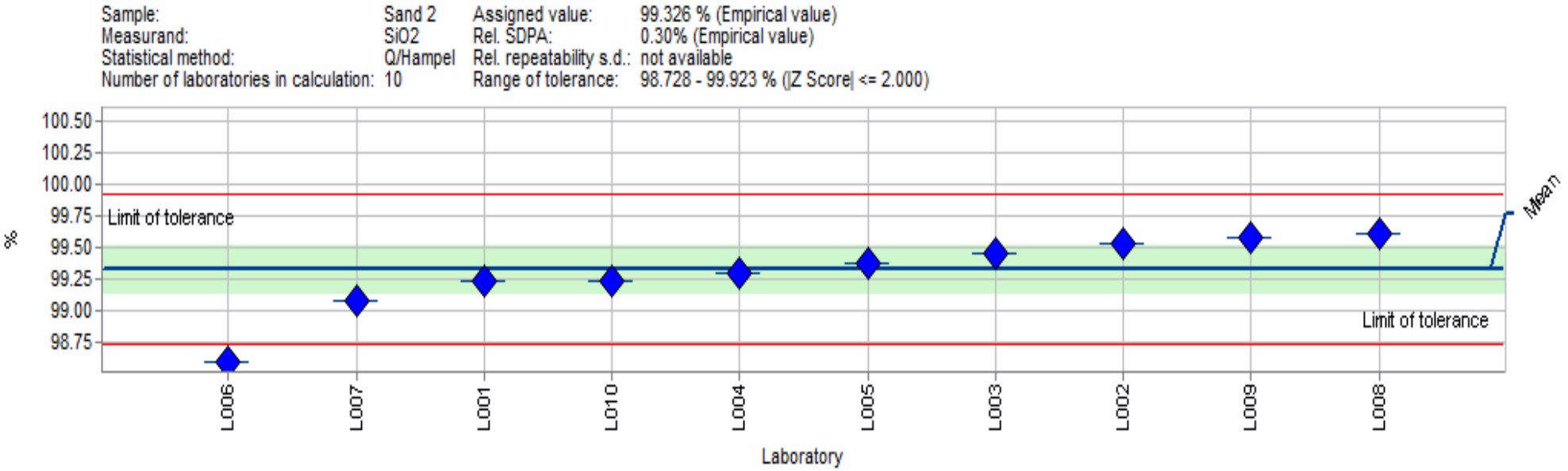


Table 28: Sand Sample – 2 Measurand Al_2O_3

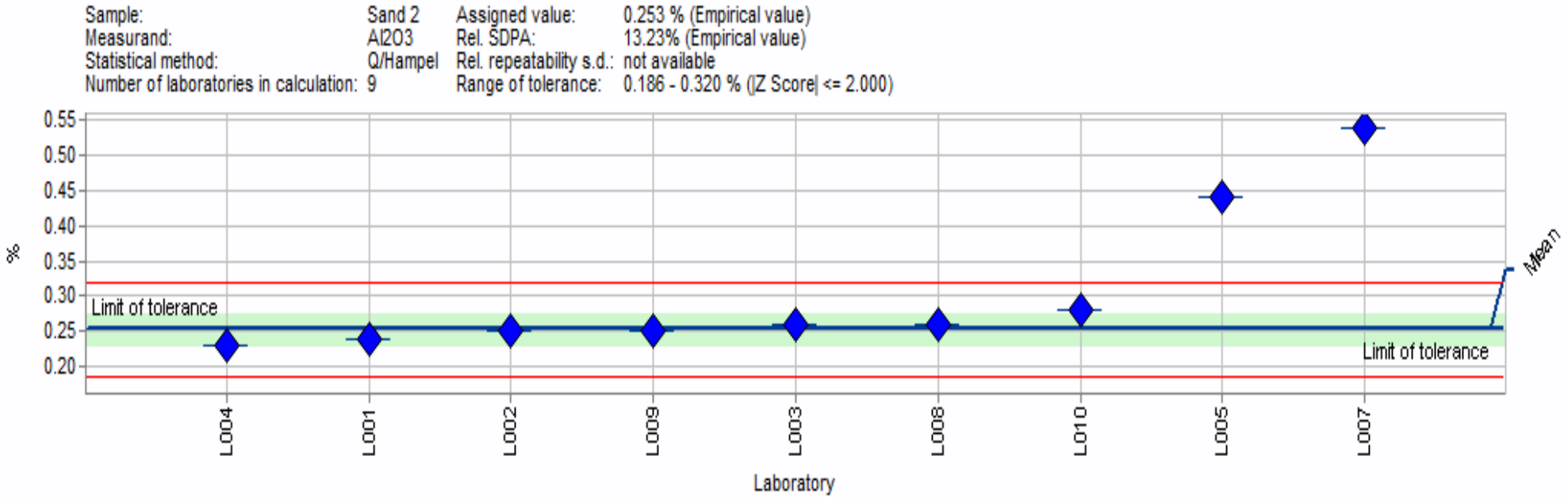


Table 29: Sand Sample – 2 Measurand Fe_2O_3

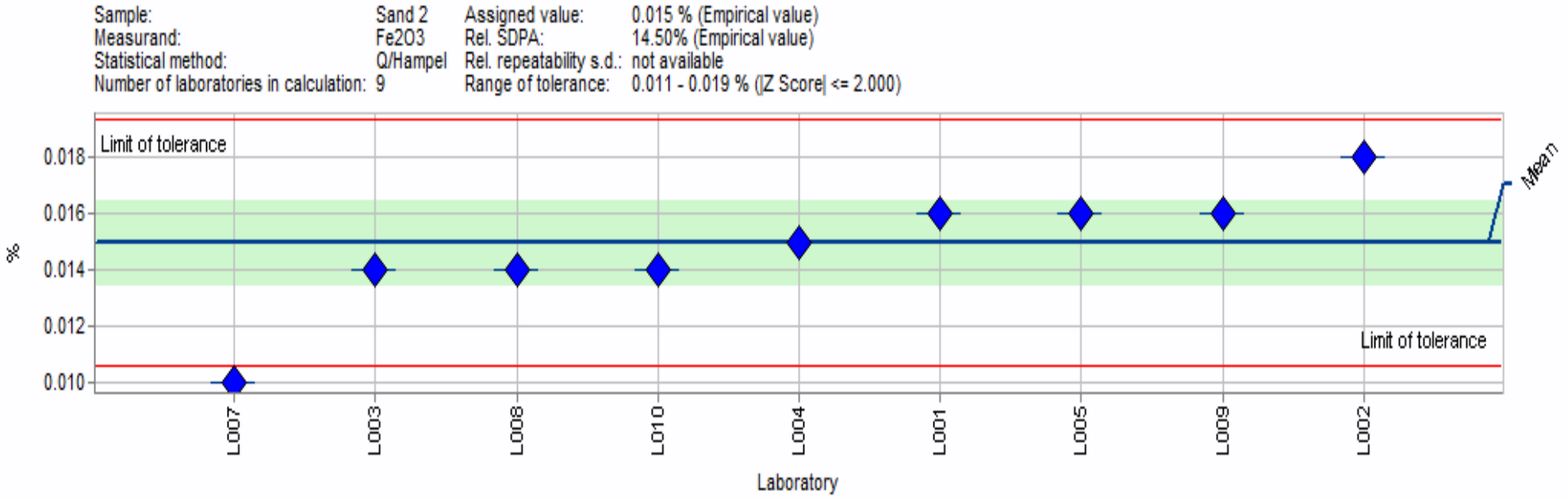


Table 30: Sand Sample – 2 Measurand TiO_2

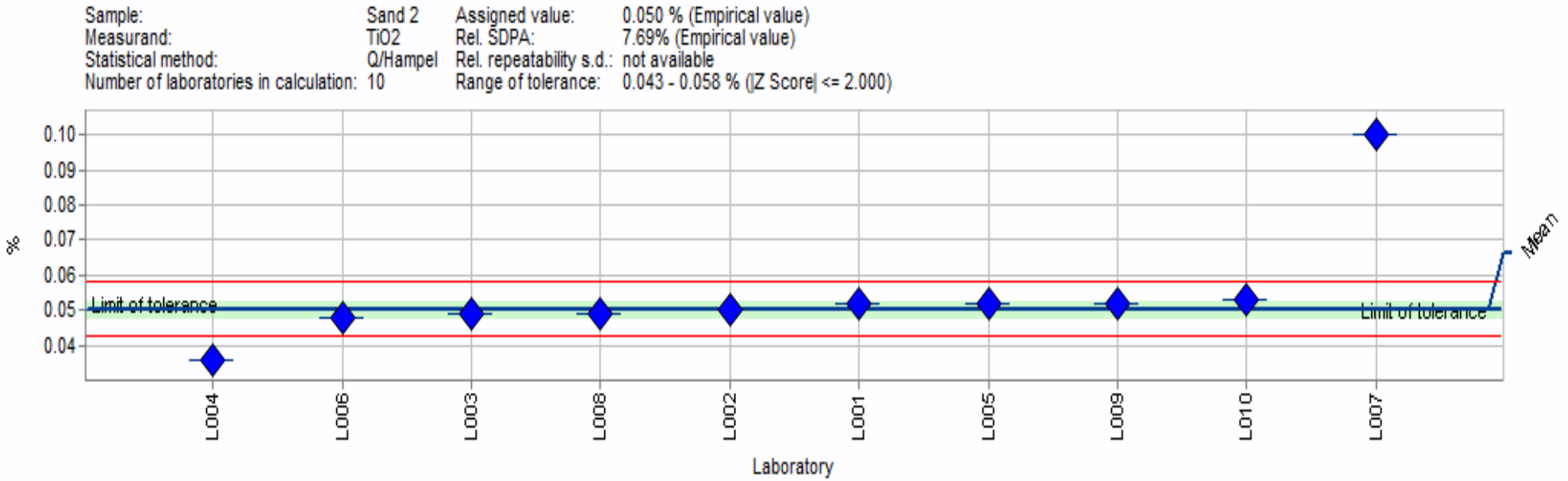


Table 31: Sand Sample – 2 Measurand CaO

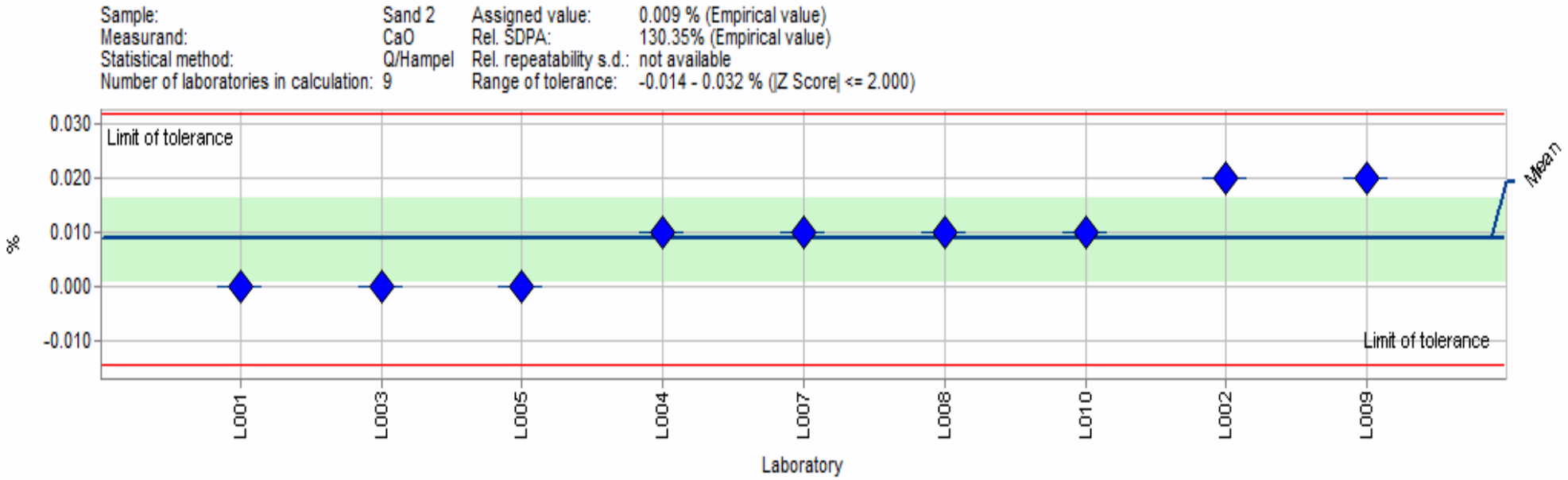


Table 32: Sand Sample – 2 Measurand MgO

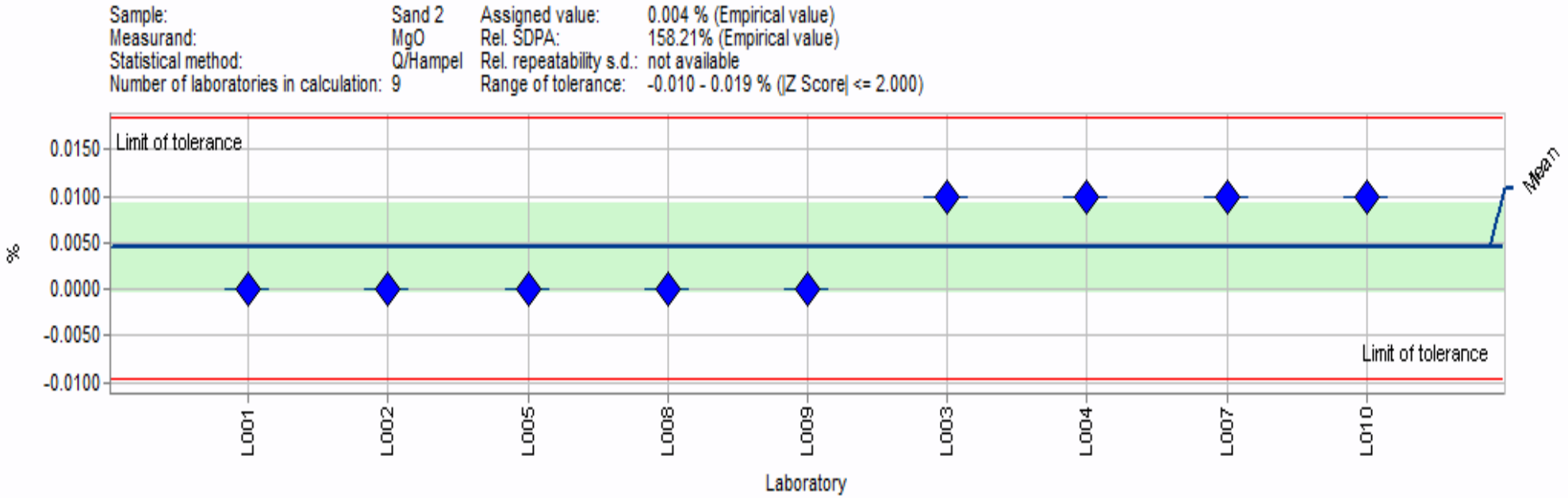


Table 33: Sand Sample – 2 Measurand Na_2O

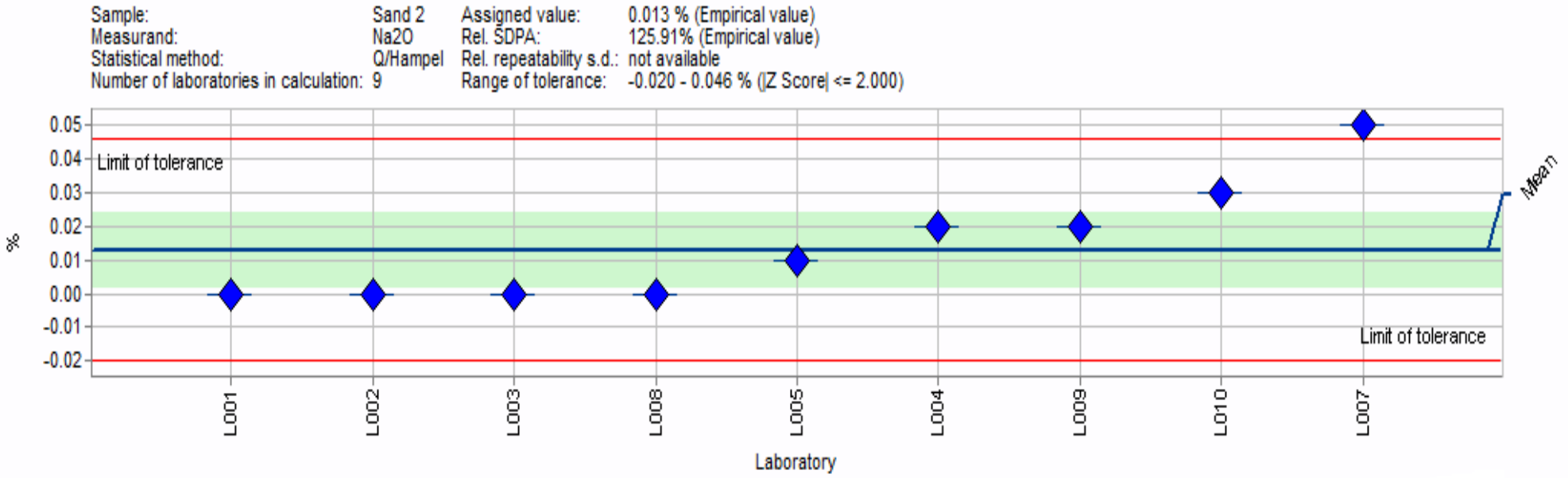
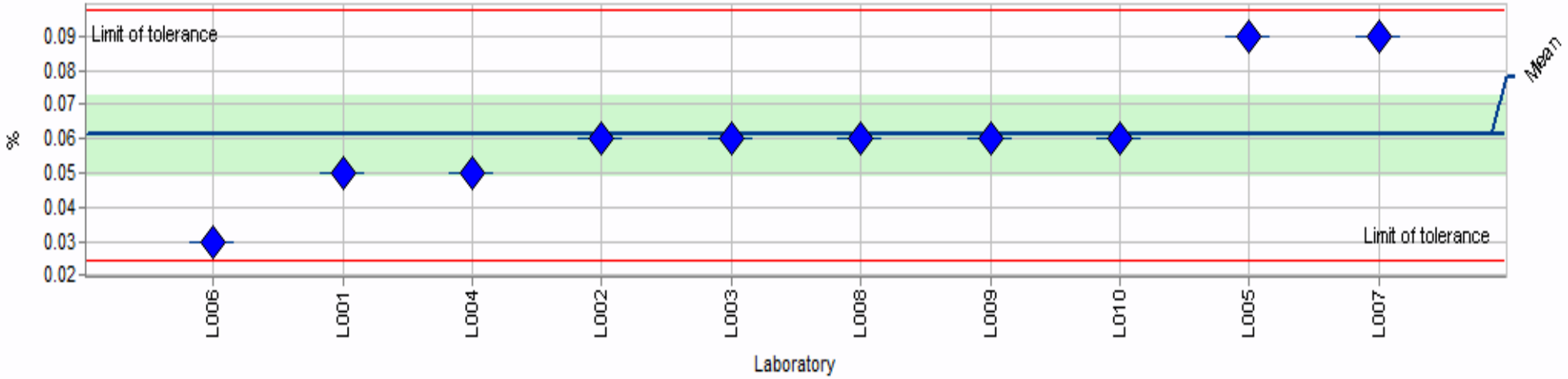


Table 34: Sand Sample – 2 Measurand K_2O

Sample:	Sand 2	Assigned value:	0.061 % (Empirical value)
Measurand:	K2O	Rel. SDPA:	29.87% (Empirical value)
Statistical method:	Q/Hampel	Rel. repeatability s.d.:	not available
Number of laboratories in calculation:	10	Range of tolerance:	0.025 - 0.098 % (|Z Score| <= 2.000)



6.5. Chart of Z-scores of all laboratories by measurand

Table 35: Measurand SiO_2

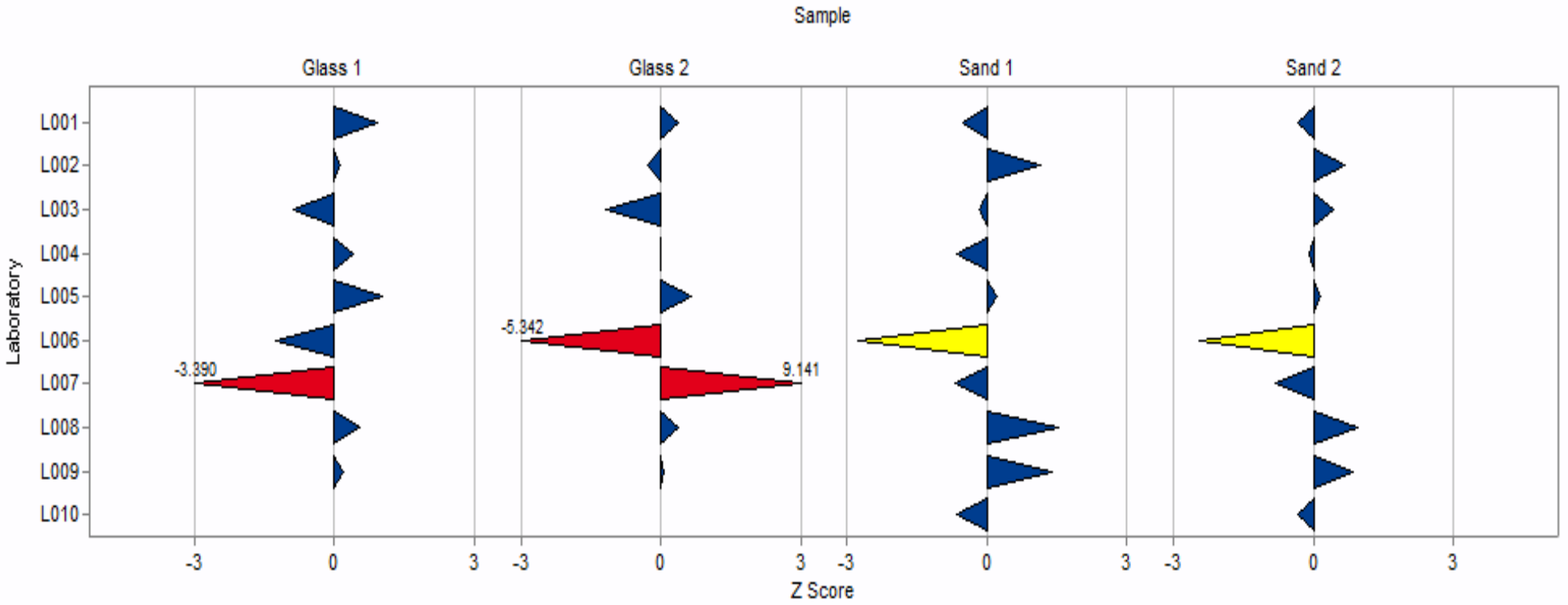


Table 36: Measurand Al_2O_3

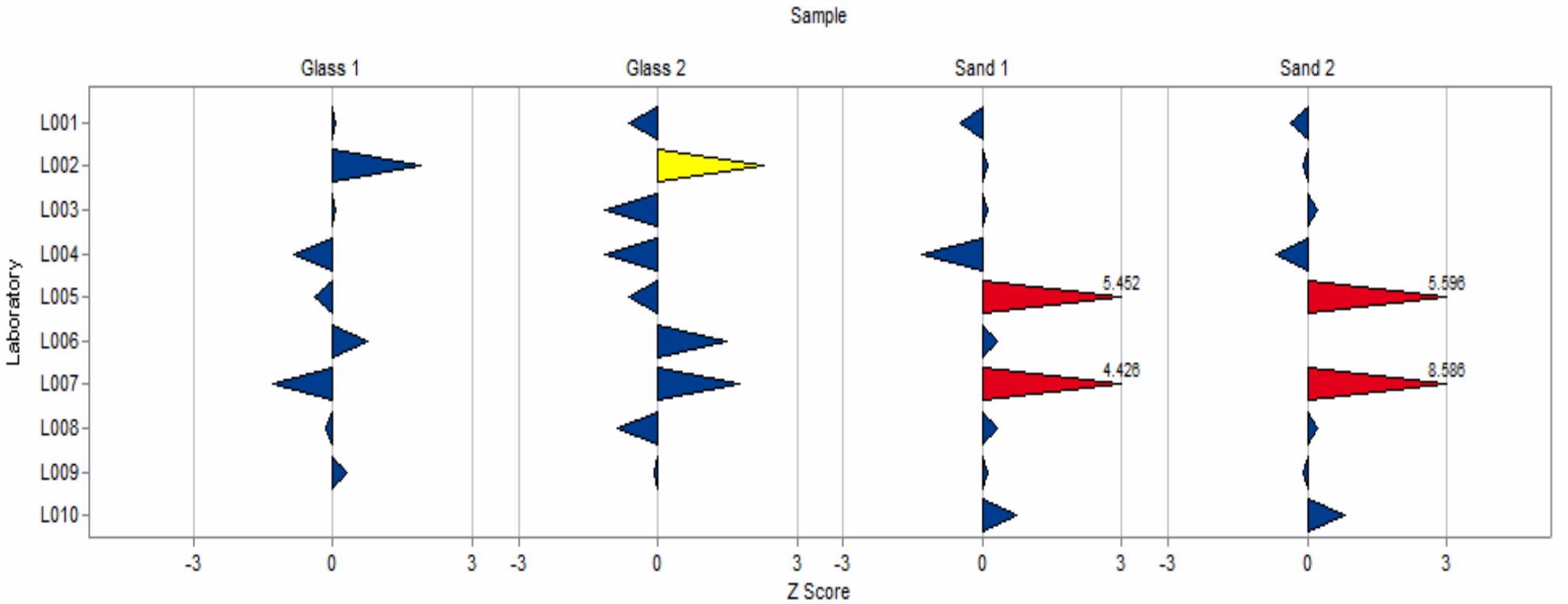


Table 37: Measurand Fe_2O_3

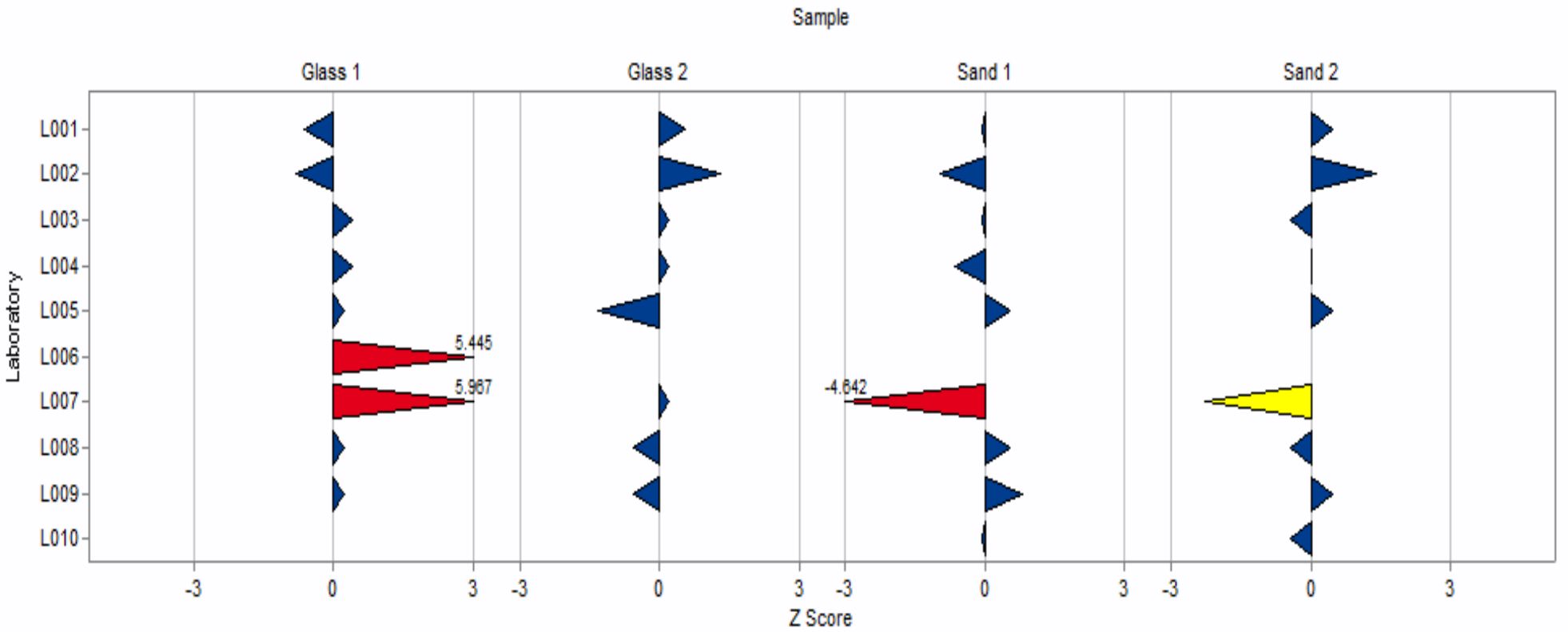


Table 38: Measurand TiO_2

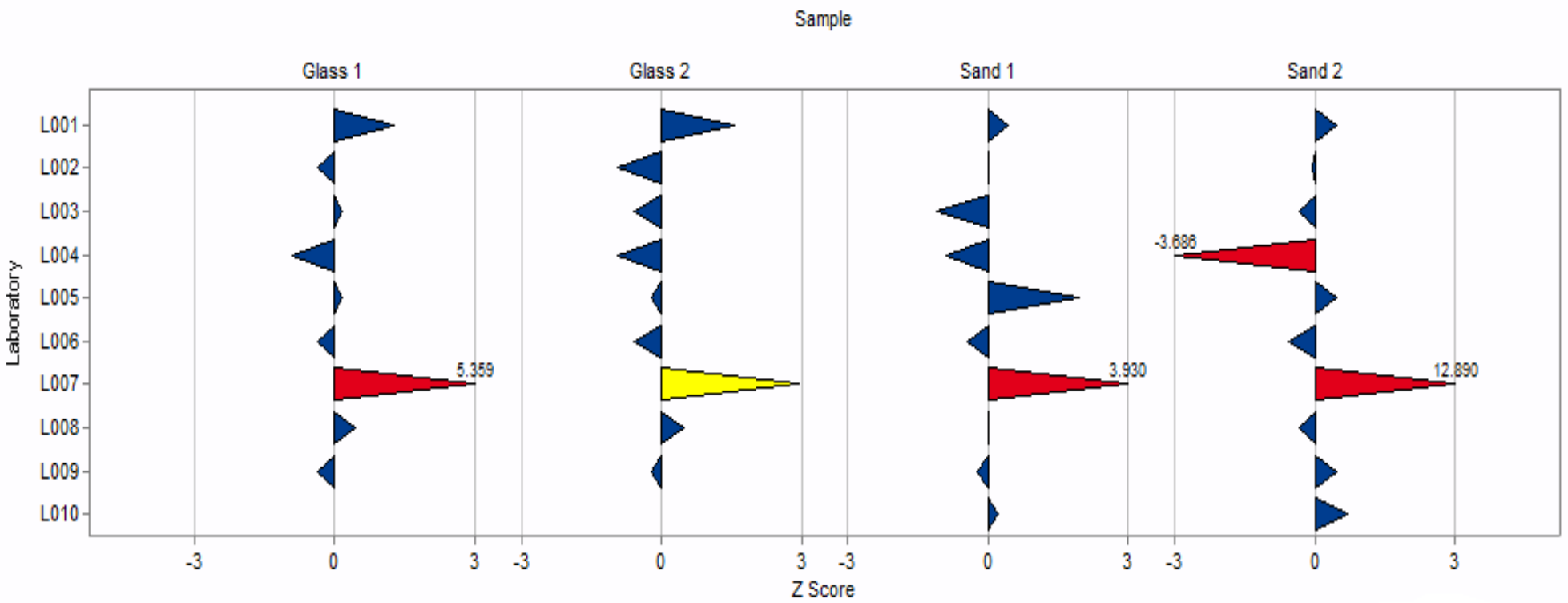


Table 39: Measurand CaO

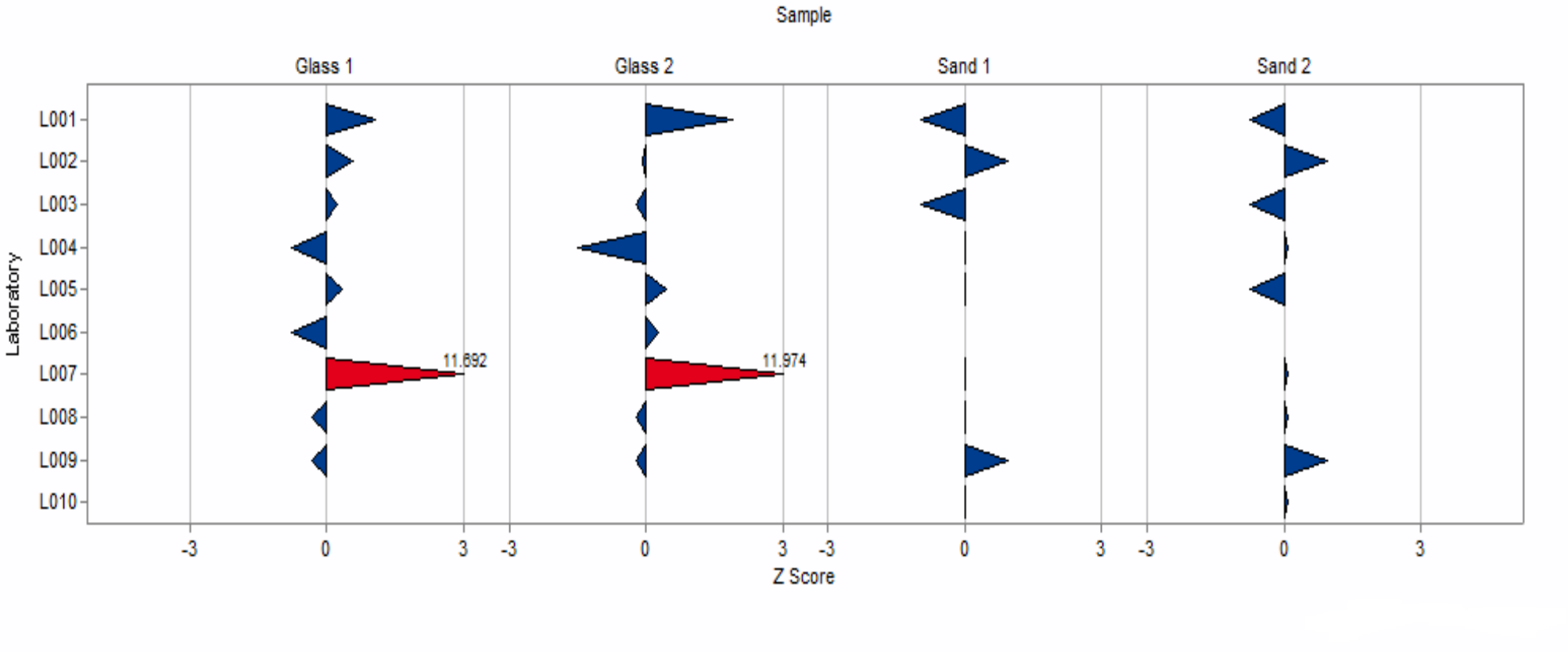


Table 40: Measurand MgO

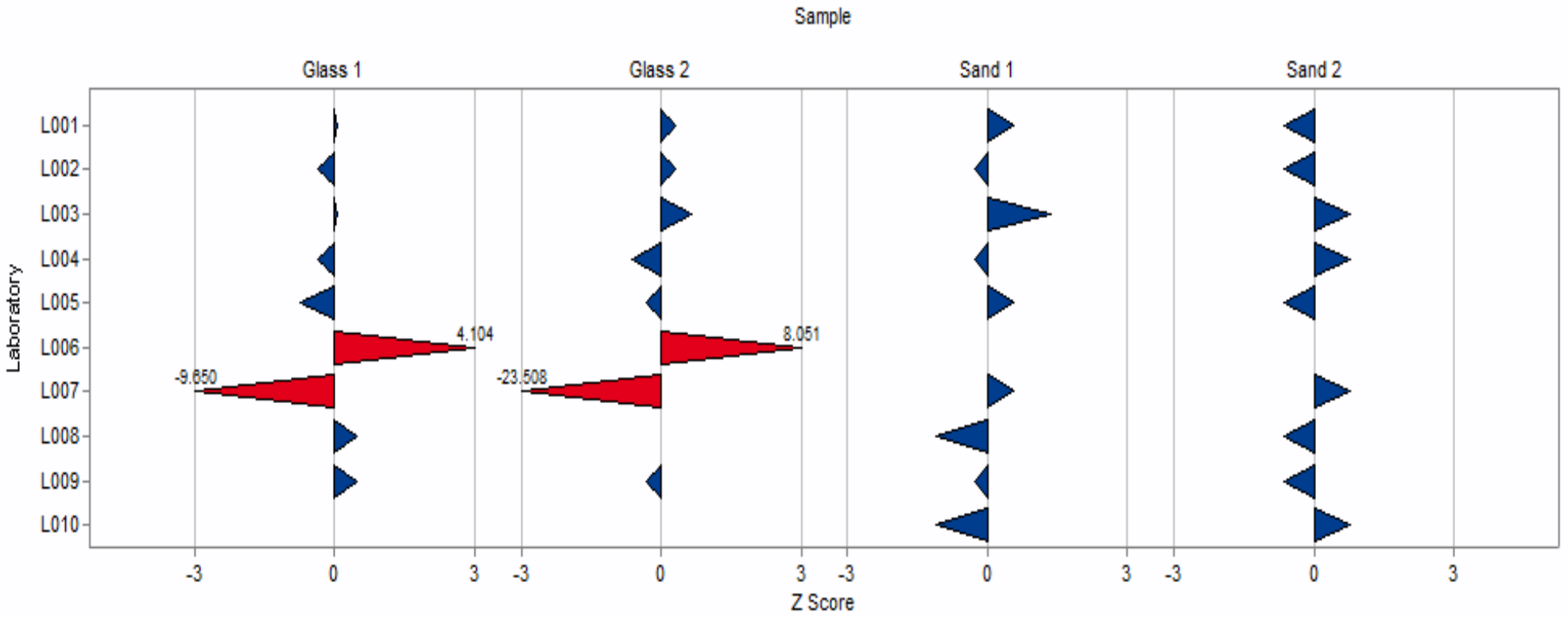


Table 41: Measurand Na_2O

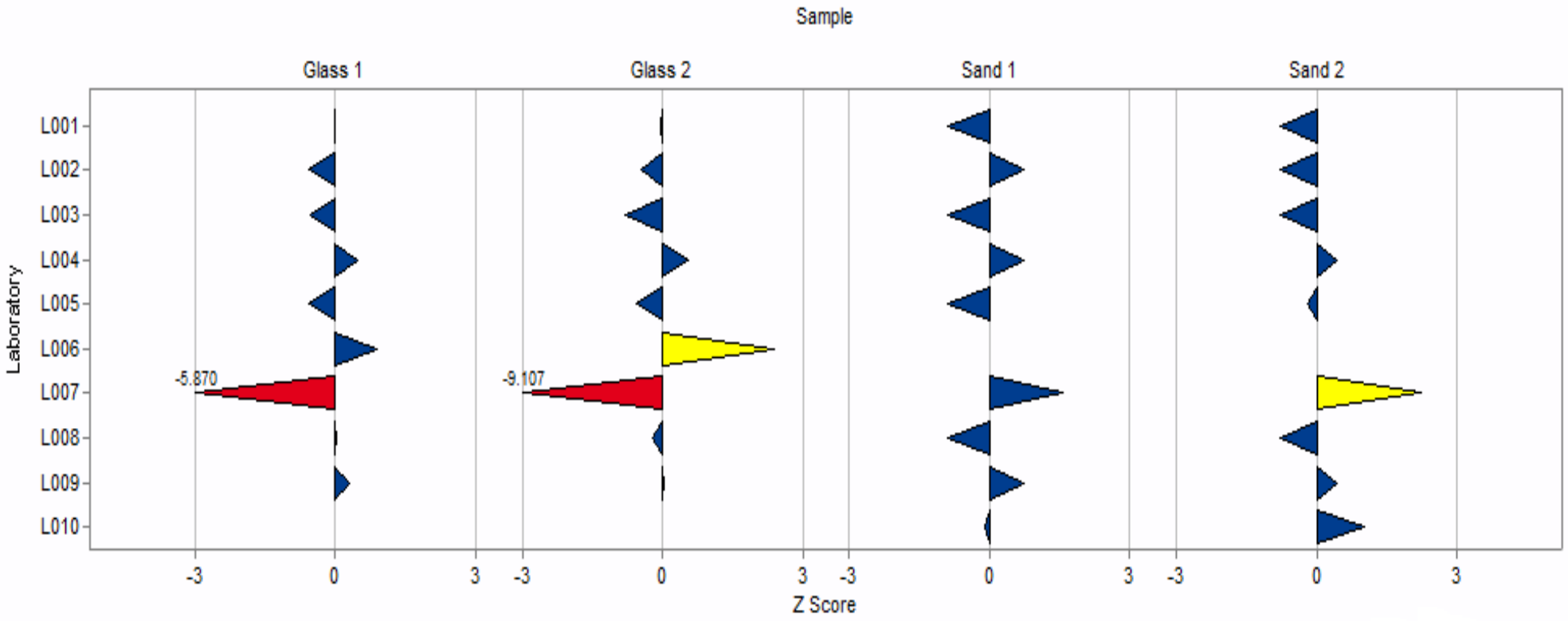


Table 42: Measurand K_2O

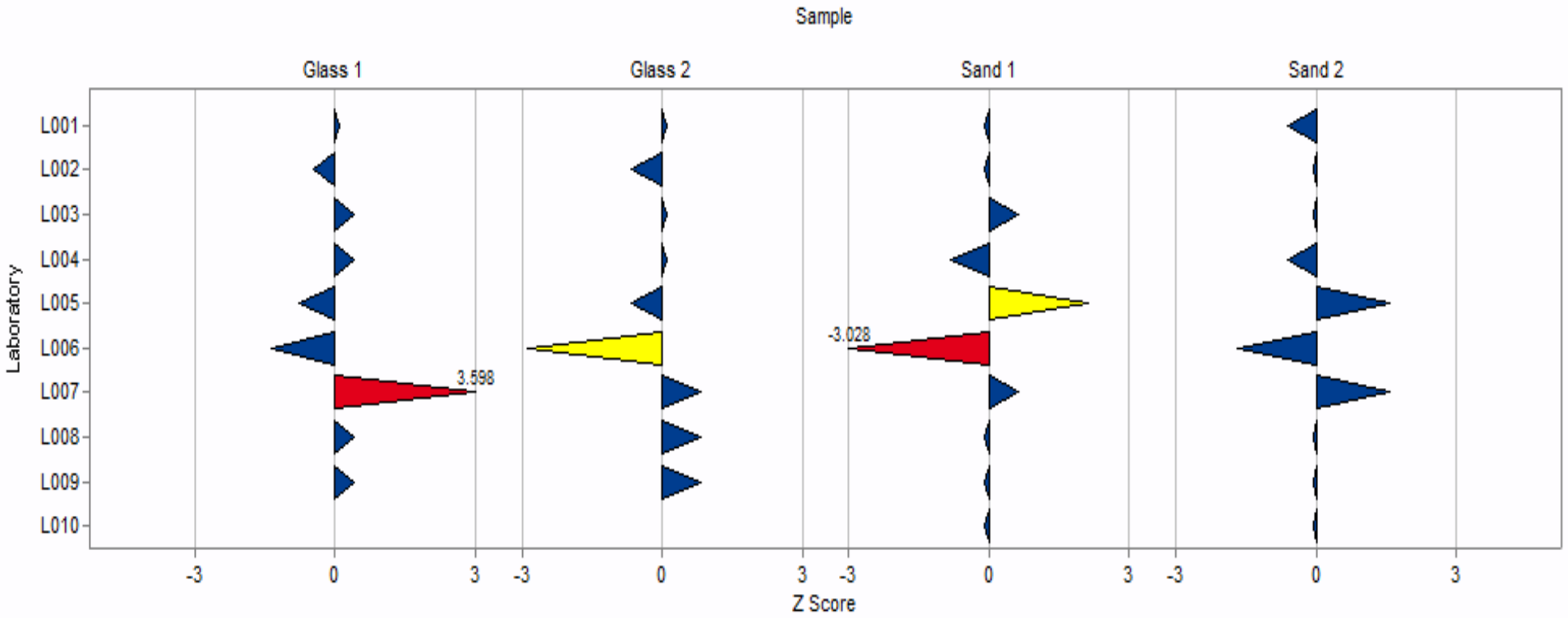
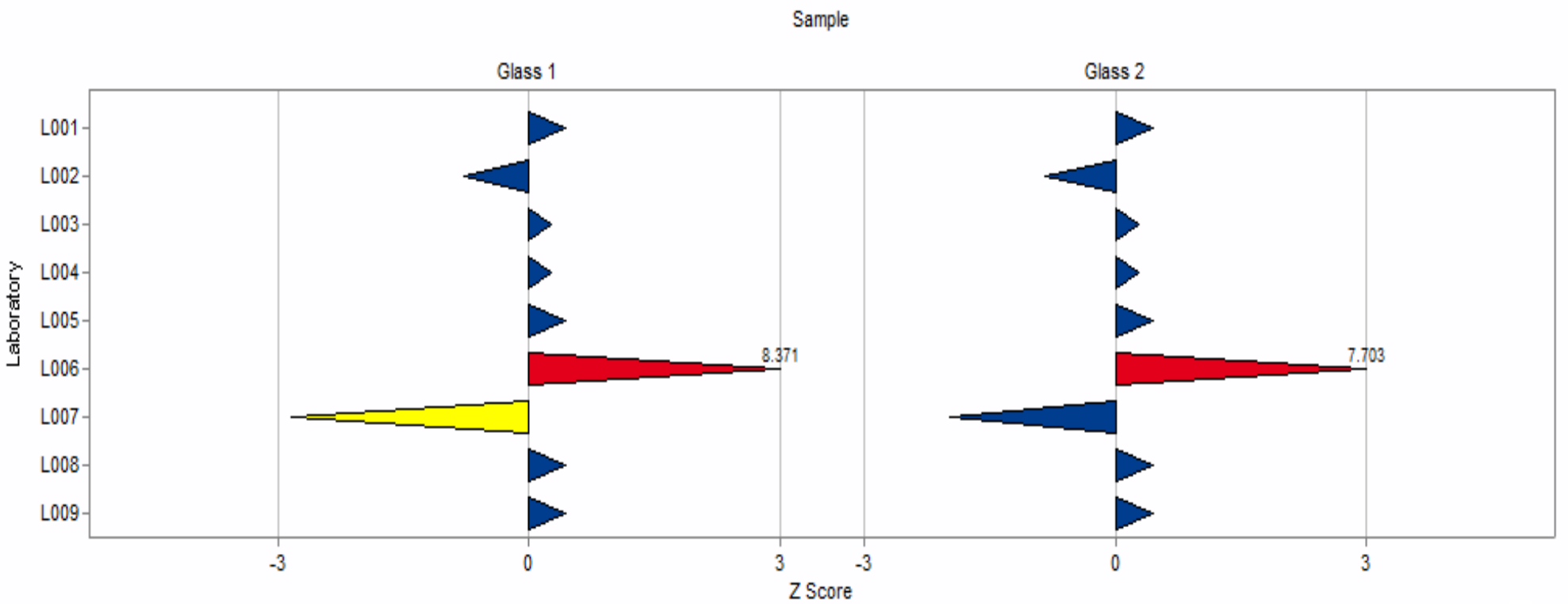


Table 43: Measurand SO_3



6.6. Descriptive Statistics

Table 44: Measurand SiO_2

Summary of laboratory test results

Measurand SiO2

	GLASS1	Z score	GLASS2	Z score	SAND1	Z score	SAND2	Z score
Unit	%		%		%		%	
L001	71.820	0.931	72.060	0.379	98.630	-0.531	99.230	-0.320
L002	71.520	0.135	71.800	-0.291	99.010	1.133	99.530	0.683
L003	71.140	-0.872	71.450	-1.193	98.710	-0.181	99.450	0.416
L004	71.620	0.401	71.910	-0.007	98.600	-0.662	99.300	-0.086
L005	71.860	1.037	72.170	0.663	98.800	0.214	99.370	0.148
L006	70.990	-1.269	69.840	-5.342	98.120	-2.765	98.590	-2.462
L007	70.190	-3.390	75.460	9.141	98.590	-0.706	99.080	-0.822
L008	71.680	0.560	72.060	0.379	99.100	1.528	99.610	0.951
L009	71.540	0.188	71.940	0.070	99.070	1.396	99.580	0.851
L010					98.600	-0.662	99.230	-0.320
–	–	–	–	–	–	–	–	–
Statistical method	Q/Hampel		Q/Hampel		Q/Hampel		Q/Hampel	
Assessment	|Z|<=2.000		|Z|<=2.000		|Z|<=2.000		|Z|<=2.000	
No. of laboratories that submitted results	9		9		10		10	
No. of participants (according to design)	10		10		10		10	
Assigned value	71.469		71.913		98.751		99.326	
Mean	71.469		71.913		98.751		99.326	
SDPA	0.377		0.388		0.228		0.299	
Reproducibility s.d.	0.377		0.388		0.228		0.299	
Rel. SDPA	0.53 %		0.54 %		0.23 %		0.30 %	
Rel. reproducibility s.d.	0.53 %		0.54 %		0.23 %		0.30 %	
Lower limit of tolerance	70.714		71.137		98.295		98.728	
Upper limit of tolerance	72.223		72.689		99.208		99.923	
Standard error	0.126		0.129		0.072		0.095	
Lower confidence limit	71.217		71.654		98.607		99.137	
Upper confidence limit	71.720		72.172		98.896		99.515	

Table 45: Measurand Al_2O_3

Summary of laboratory test results

Measurand Al2O3

	GLASS1	Z score	GLASS2	Z score	SAND1	Z score	SAND2	Z score
Unit	%		%		%		%	
L001	1.150	0.069	1.480	-0.618	0.550	-0.496	0.240	-0.384
L002	1.230	1.891	1.590	2.292	0.580	0.119	0.250	-0.085
L003	1.150	0.069	1.460	-1.147	0.580	0.119	0.260	0.214
L004	1.110	-0.842	1.460	-1.147	0.510	-1.317	0.230	-0.683
L005	1.130	-0.387	1.480	-0.618	0.840	5.452	0.440	5.596
L006	1.180	0.752	1.560	1.499	0.590	0.324		
L007	1.090	-1.298	1.570	1.763	0.790	4.426	0.540	8.586
L008	1.140	-0.159	1.470	-0.882	0.590	0.324	0.260	0.214
L009	1.160	0.296	1.500	-0.088	0.580	0.119	0.250	-0.085
L010					0.610	0.734	0.280	0.812
–	–	–	–	–	–	–	–	–
Statistical method	Q/Hampel		Q/Hampel		Q/Hampel		Q/Hampel	
Assessment	|Z|<=2.000		|Z|<=2.000		|Z|<=2.000		|Z|<=2.000	
No. of laboratories that submitted results	9		9		10		9	
No. of participants (according to design)	10		10		10		10	
Assigned value	1.147		1.503		0.574		0.253	
Mean	1.147		1.503		0.574		0.253	
SDPA	0.044		0.038		0.049		0.033	
Reproducibility s.d.	0.044		0.038		0.049		0.033	
Rel. SDPA	3.83 %		2.51 %		8.49 %		13.23 %	
Rel. reproducibility s.d.	3.83 %		2.51 %		8.49 %		13.23 %	
Lower limit of tolerance	1.059		1.428		0.477		0.186	
Upper limit of tolerance	1.235		1.579		0.672		0.320	
Standard error	0.015		0.013		0.015		0.011	
Lower confidence limit	1.118		1.478		0.543		0.231	
Upper confidence limit	1.176		1.529		0.605		0.275	

Table 46: Measurand Fe_2O_3

Summary of laboratory test results

Measurand Fe2O3

	GLASS1	Z score	GLASS2	Z score	SAND1	Z score	SAND2	Z score
Unit	%		%		%		%	
L001	0.068	-0.646	0.021	0.562	0.055	-0.074	0.016	0.476
L002	0.067	-0.820	0.023	1.312	0.049	-0.958	0.018	1.397
L003	0.074	0.398	0.020	0.187	0.055	-0.074	0.014	-0.446
L004	0.074	0.398	0.020	0.187	0.051	-0.663	0.015	0.015
L005	0.073	0.224	0.016	-1.312	0.059	0.516	0.016	0.476
L006	0.103	5.445						
L007	0.106	5.967	0.020	0.187	0.024	-4.642	0.010	-2.289
L008	0.073	0.224	0.018	-0.562	0.059	0.516	0.014	-0.446
L009	0.073	0.224	0.018	-0.562	0.061	0.811	0.016	0.476
L010					0.055	-0.074	0.014	-0.446
–	–	–	–	–	–	–	–	–
Statistical method	Q/Hampel		Q/Hampel		Q/Hampel		Q/Hampel	
Assessment	|Z|<=2.000		|Z|<=2.000		|Z|<=2.000		|Z|<=2.000	
No. of laboratories that submitted results	9		8		9		9	
No. of participants (according to design)	10		10		10		10	
Assigned value	0.072		0.020		0.056		0.015	
Mean	0.072		0.020		0.056		0.015	
SDPA	0.006		0.003		0.007		0.002	
Reproducibility s.d.	0.006		0.003		0.007		0.002	
Rel. SDPA	8.01 %		13.68 %		12.23 %		14.50 %	
Rel. reproducibility s.d.	8.01 %		13.68 %		12.23 %		14.50 %	
Lower limit of tolerance	0.060		0.014		0.042		0.011	
Upper limit of tolerance	0.083		0.025		0.069		0.019	
Standard error	0.002		0.001		0.002		0.001	
Lower confidence limit	0.068		0.018		0.051		0.014	
Upper confidence limit	0.076		0.021		0.060		0.016	

Table 47: Measurand TiO_2

Summary of laboratory test results

Measurand TiO2

	GLASS1	Z score	GLASS2	Z score	SAND1	Z score	SAND2	Z score
Unit	%		%		%		%	
L001	0.053	1.263	0.046	1.544	0.095	0.426	0.052	0.458
L002	0.047	-0.375	0.039	-0.934	0.093	-0.012	0.050	-0.060
L003	0.049	0.171	0.040	-0.580	0.088	-1.107	0.049	-0.319
L004	0.045	-0.922	0.039	-0.934	0.089	-0.888	0.036	-3.686
L005	0.049	0.171	0.041	-0.226	0.102	1.959	0.052	0.458
L006	0.047	-0.375	0.040	-0.580	0.091	-0.450	0.048	-0.578
L007	0.068	5.359	0.050	2.959	0.111	3.930	0.100	12.890
L008	0.050	0.444	0.043	0.482	0.093	-0.012	0.049	-0.319
L009	0.047	-0.375	0.041	-0.226	0.092	-0.231	0.052	0.458
L010					0.094	0.207	0.053	0.717
–	–	–	–	–	–	–	–	–
Statistical method	Q/Hampel		Q/Hampel		Q/Hampel		Q/Hampel	
Assessment	|Z|<=2.000		|Z|<=2.000		|Z|<=2.000		|Z|<=2.000	
No. of laboratories that submitted results	9		9		10		10	
No. of participants (according to design)	10		10		10		10	
Assigned value	0.048		0.042		0.093		0.050	
Mean	0.048		0.042		0.093		0.050	
SDPA	0.004		0.003		0.005		0.004	
Reproducibility s.d.	0.004		0.003		0.005		0.004	
Rel. SDPA	7.57 %		6.78 %		4.91 %		7.69 %	
Rel. reproducibility s.d.	7.57 %		6.78 %		4.91 %		7.69 %	
Lower limit of tolerance	0.041		0.036		0.084		0.043	
Upper limit of tolerance	0.056		0.047		0.102		0.058	
Standard error	0.001		0.001		0.001		0.001	
Lower confidence limit	0.046		0.040		0.090		0.048	
Upper confidence limit	0.051		0.044		0.096		0.053	

Table 48: Measurand CaO

Summary of laboratory test results

Measurand CaO

	GLASS1	Z score	GLASS2	Z score	SAND1	Z score	SAND2	Z score
Unit	%		%		%		%	
L001	8.810	1.060	8.570	1.892	0.000	-0.954	0.000	-0.767
L002	8.730	0.582	8.340	-0.057	0.020	0.954	0.020	0.959
L003	8.670	0.224	8.320	-0.226	0.000	-0.954	0.000	-0.767
L004	8.500	-0.791	8.170	-1.497	0.010	0.000	0.010	0.096
L005	8.690	0.343	8.400	0.451	0.010	0.000	0.000	-0.767
L006	8.500	-0.791	8.380	0.282				
L007	10.590	11.692	9.760	11.974	0.010	0.000	0.010	0.096
L008	8.580	-0.314	8.320	-0.226	0.010	0.000	0.010	0.096
L009	8.580	-0.314	8.320	-0.226	0.020	0.954	0.020	0.959
L010					0.010	0.000	0.010	0.096
–	–	–	–	–	–	–	–	–
Statistical method	Q/Hampel		Q/Hampel		Q/Hampel		Q/Hampel	
Assessment	|Z|<=2.000		|Z|<=2.000		|Z|<=2.000		|Z|<=2.000	
No. of laboratories that submitted results	9		9		9		9	
No. of participants (according to design)	10		10		10		10	
Assigned value	8.633		8.347		0.010		0.009	
Mean	8.633		8.347		0.010		0.009	
SDPA	0.167		0.118		0.010		0.012	
Reproducibility s.d.	0.167		0.118		0.010		0.012	
Rel. SDPA	1.94 %		1.41 %		104.84 %		130.35 %	
Rel. reproducibility s.d.	1.94 %		1.41 %		104.84 %		130.35 %	
Lower limit of tolerance	8.298		8.111		-0.011		-0.014	
Upper limit of tolerance	8.967		8.583		0.031		0.032	
Standard error	0.056		0.039		0.003		0.004	
Lower confidence limit	8.521		8.268		0.003		0.001	
Upper confidence limit	8.744		8.425		0.017		0.017	

Table 49: Measurand MgO

Summary of laboratory test results

Measurand MgO

	GLASS1	Z score	GLASS2	Z score	SAND1	Z score	SAND2	Z score
Unit	%		%		%		%	
L001	4.280	0.059	3.460	0.322	0.030	0.549	0.000	-0.632
L002	4.270	-0.345	3.460	0.322	0.020	-0.274	0.000	-0.632
L003	4.280	0.059	3.470	0.644	0.040	1.372	0.010	0.790
L004	4.270	-0.345	3.430	-0.644	0.020	-0.274	0.010	0.790
L005	4.260	-0.750	3.440	-0.322	0.030	0.549	0.000	-0.632
L006	4.380	4.104	3.700	8.051				
L007	4.040	-9.650	2.720	-23.508	0.030	0.549	0.010	0.790
L008	4.290	0.464	3.450	0.000	0.010	-1.098	0.000	-0.632
L009	4.290	0.464	3.440	-0.322	0.020	-0.274	0.000	-0.632
L010					0.010	-1.098	0.010	0.790
–	–	–	–	–	–	–	–	–
Statistical method	Q/Hampel		Q/Hampel		Q/Hampel		Q/Hampel	
Assessment	|Z|<=2.000		|Z|<=2.000		|Z|<=2.000		|Z|<=2.000	
No. of laboratories that submitted results	9		9		9		9	
No. of participants (according to design)	10		10		10		10	
Assigned value	4.279		3.450		0.023		0.004	
Mean	4.279		3.450		0.023		0.004	
SDPA	0.025		0.031		0.012		0.007	
Reproducibility s.d.	0.025		0.031		0.012		0.007	
Rel. SDPA	0.58 %		0.90 %		52.06 %		158.21 %	
Rel. reproducibility s.d.	0.58 %		0.90 %		52.06 %		158.21 %	
Lower limit of tolerance	4.229		3.388		-0.001		-0.010	
Upper limit of tolerance	4.328		3.512		0.048		0.019	
Standard error	0.008		0.010		0.004		0.002	
Lower confidence limit	4.262		3.429		0.015		0.000	
Upper confidence limit	4.295		3.471		0.031		0.009	

Table 50: Measurand Na_2O

Summary of laboratory test results

Measurand Na2O

	GLASS1	Z score	GLASS2	Z score	SAND1	Z score	SAND2	Z score
Unit	%		%		%		%	
L001	13.550	-0.018	14.390	-0.032	0.000	-0.904	0.000	-0.794
L002	13.330	-0.550	14.190	-0.451	0.020	0.734	0.000	-0.794
L003	13.340	-0.526	14.020	-0.807	0.000	-0.904	0.000	-0.794
L004	13.750	0.465	14.660	0.534	0.020	0.734	0.020	0.419
L005	13.330	-0.550	14.140	-0.556	0.000	-0.904	0.010	-0.188
L006	13.920	0.877	15.540	2.379				
L007	11.130	-5.870	10.060	-9.107	0.030	1.553	0.050	2.239
L008	13.560	0.006	14.300	-0.220	0.000	-0.904	0.000	-0.794
L009	13.680	0.296	14.420	0.031	0.020	0.734	0.020	0.419
L010					0.010	-0.085	0.030	1.026
–	–	–	–	–	–	–	–	–
Statistical method	Q/Hampel		Q/Hampel		Q/Hampel		Q/Hampel	
Assessment	|Z|<=2.000		|Z|<=2.000		|Z|<=2.000		|Z|<=2.000	
No. of laboratories that submitted results	9		9		9		9	
No. of participants (according to design)	10		10		10		10	
Assigned value	13.558		14.405		0.011		0.013	
Mean	13.558		14.405		0.011		0.013	
SDPA	0.414		0.477		0.012		0.016	
Reproducibility s.d.	0.414		0.477		0.012		0.016	
Rel. SDPA	3.05 %		3.31 %		110.60 %		125.91 %	
Rel. reproducibility s.d.	3.05 %		3.31 %		110.60 %		125.91 %	
Lower limit of tolerance	12.730		13.451		-0.013		-0.020	
Upper limit of tolerance	14.385		15.359		0.035		0.046	
Standard error	0.138		0.159		0.004		0.005	
Lower confidence limit	13.282		14.087		0.003		0.002	
Upper confidence limit	13.833		14.723		0.019		0.024	

Table 51: Measurand K_2O

Summary of laboratory test results

Measurand K2O

	GLASS1	Z score	GLASS2	Z score	SAND1	Z score	SAND2	Z score
Unit	%		%		%		%	
L001	0.400	0.106	0.060	0.094	0.140	-0.095	0.050	-0.606
L002	0.380	-0.477	0.050	-0.652	0.140	-0.095	0.060	-0.058
L003	0.410	0.397	0.060	0.094	0.150	0.638	0.060	-0.058
L004	0.410	0.397	0.060	0.094	0.130	-0.828	0.050	-0.606
L005	0.370	-0.768	0.050	-0.652	0.170	2.104	0.090	1.587
L006	0.350	-1.350	0.020	-2.890	0.100	-3.028	0.030	-1.703
L007	0.520	3.598	0.070	0.840	0.150	0.638	0.090	1.587
L008	0.410	0.397	0.070	0.840	0.140	-0.095	0.060	-0.058
L009	0.410	0.397	0.070	0.840	0.140	-0.095	0.060	-0.058
L010					0.140	-0.095	0.060	-0.058
–	–	–	–	–	–	–	–	–
Statistical method	Q/Hampel		Q/Hampel		Q/Hampel		Q/Hampel	
Assessment	|Z|<=2.000		|Z|<=2.000		|Z|<=2.000		|Z|<=2.000	
No. of laboratories that submitted results	9		9		10		10	
No. of participants (according to design)	10		10		10		10	
Assigned value	0.396		0.059		0.141		0.061	
Mean	0.396		0.059		0.141		0.061	
SDPA	0.034		0.013		0.014		0.018	
Reproducibility s.d.	0.034		0.013		0.014		0.018	
Rel. SDPA	8.67 %		22.82 %		9.65 %		29.87 %	
Rel. reproducibility s.d.	8.67 %		22.82 %		9.65 %		29.87 %	
Lower limit of tolerance	0.328		0.032		0.114		0.025	
Upper limit of tolerance	0.465		0.086		0.169		0.098	
Standard error	0.011		0.004		0.004		0.006	
Lower confidence limit	0.373		0.050		0.133		0.050	
Upper confidence limit	0.419		0.068		0.150		0.073	

Table 52: Measurand SO_3

Summary of laboratory test results

Measurand SO3

	GLASS1	Z score	GLASS2	Z score
Unit	%		%	
L001	0.220	0.436	0.250	0.445
L002	0.150	-0.771	0.170	-0.846
L003	0.210	0.264	0.240	0.283
L004	0.210	0.264	0.240	0.283
L005	0.220	0.436	0.250	0.445
L006	0.680	8.371	0.700	7.703
L007	0.030	-2.842	0.100	-1.975
L008	0.220	0.436	0.250	0.445
L009	0.220	0.436	0.250	0.445
–	–	–	–	–
Statistical method	Q/Hampel		Q/Hampel	
Assessment	|Z|<=2.000		|Z|<=2.000	
No. of laboratories that submitted results	9		9	
No. of participants (according to design)	10		10	
Assigned value	0.195		0.222	
Mean	0.195		0.222	
SDPA	0.058		0.062	
Reproducibility s.d.	0.058		0.062	
Rel. SDPA	29.77 %		27.87 %	
Rel. reproducibility s.d.	29.77 %		27.87 %	
Lower limit of tolerance	0.079		0.098	
Upper limit of tolerance	0.311		0.346	
Standard error	0.019		0.021	
Lower confidence limit	0.156		0.181	
Upper confidence limit	0.233		0.264	

8. REFERENCES

- ISO/IEC 17043:2010, Conformity assessment – General requirements for proficiency testing.
- ISO 13528:2015, 2nd Edition, Statistical methods for use in proficiency testing by interlaboratory comparison.
- Duewer, D.L., A comparison of location estimators for interlaboratory data contaminated with value and uncertainty outliers', Accred.Qual.Assur., 2008, 13, 193-216.
- The International Harmonized Protocol for Proficiency Testing of Analytical Chemistry Laboratories (IUPAC Technical Report) 2006
- ISO/IEC 17043:2010 Conformity assessment -- General requirements for proficiency testing
- ISO 5725 Accuracy (trueness and precision) of measurement methods and results
- Analysis of Extreme Values – W.J.Dixon
- Simplified Statistics for Small Numbers of Observations – R.B.Dean and W.J.Dixon
- Ratios Involving Extreme Values – W.J.Dixon
- Programs to Compute Distribution Functions and Critical Values for Extreme Value Ratios for Outlier Detection – George C. McBane