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Proficiency testing provider

Report

(final)

on the evaluation of the proficiency testing programme

PT 32/9A (*RM S-4A*)

**Determination of Mn, C, Si, P, S
in ferromanganese by X-Ray Fluorescence spectrometries and wet-
way analysis, S on combustion analysers by IR absorption**

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1. General information on PT (table 1)

Label	PT 32/9A
Object of PT	Determination of Mn, C, Si, P, S in ferromanganese
Assessment method(s)	X-Ray fluorescence spectrometry and validated wet-way and for S combustion methods
Item of proficiency testing:	Ferromanganese, sample PT 32/9A
Date of testing	September-October, 2024
Name and address of the PT provider	SPL-LABMAT s.r.o. 1. máje 432, 735 31 Bohumín, www.spl-labmat.cz Tel: 596014627, e-mail: info@spl-labmat.cz
Responsible person	Ing. Martin Bogumský
Colaborator(s)	Ing. Denisa Kupczynová, René Piszczek
Operations provided by subcontractors	Providing of candidate material, preliminary chemical analysis and homogeneity analysis
Number of participants	16
Test item description	Plastic PET bottle, contents 70g
Number of test items	25 pcs crushed sample
Technique of sample preparation	Material was crushed <0.2mm, sieved and homogenised
Item and result distribution	Post and transport services, e-mail and webpages
Result acceptance	Electronic in provided forms (MS Excel files)
Performance assessment standards	Performance assessment based on z-scoring. Result z-score with $-2 \leq Z_{PT} \leq 2$ were considered satisfactory for all parameters. Reference values assessed as consensual with the values provided by participants. In all cases, this was equal to the arithmetic mean of the results after outliers exclusion by Grubbs' test. Standard deviation.
Homogeneity and stability	Material homogeneity was tested in the laboratory Enviform a.s. Measurements were done for three final samples, five determinations of each, 15 in total. For homogeneity assessments and standard deviation calculation, the statistical method ANOVA was employed for all assessments. Material homogeneity as compared with the norms for assessment of elements proved satisfactory for the PT. Homogeneity assessments were done for all elements. Given the character of the tested items, any influences of time and environment instability are excluded.

2. Confidentiality agreement

The provider of PT declares that all information and data pertinent to the individual participants are considered confidential and dealt with accordingly. Participant code numbers are assigned at random for each participant and each PT independently. In the final report, results are identified by code numbers only and are therefore anonymous.

3. Abbreviations, definitions and signs

PT proficiency testing

PT XX/XX item labelling (samples) for PT

Participant in PT

laboratory, company or private person who receives the items for PT and submits the results to the PT provider

Accepted laboratory result

laboratory result which has not been excluded as outlying

x laboratory result representing the arithmetic mean of (usually) five results submitted by participants

s selected standard deviation for five laboratory assessments for a given element

$t_{5;0,05}$ confidence level for five assessments for the reliability level 95%

u repeatability of five results for one participant, $u = \pm \frac{t_{5;0,05}}{\sqrt{5}} \cdot s$

n number of participants involved in the statistical data set after exclusion of outliers

X reference value, see 6.1 for details on assessment

X_{Ref} reference value calculated as mean of the values of selected participating laboratories

X_{PT} consensual estimate of the mean value of laboratory results performed according to a method suitable for their distribution

s_{PT} selected standard deviation from the statistical data set in PT

s_N selected standard deviation as listed in the norm for determination of the given element

Z_{PT} z-score derived from s_{PT} , see chapter 6.2

Z_N	z-score derived from s_N , see chapter 6.2
U	Uncertainty of the reference value, extended uncertainty (extension factor=2) in the sense of the ISO Guide to the Expression of the Uncertainty of Measurement (1993), dependent on the standard deviation of the laboratory results. This is expressed as a one half of a \pm interval.

4. General principles of the PT

PT was organized, executed and evaluated according to the ČSN EN ISO/IEC 17043:2010.

4.1 PT schedule

Information about the PT were made public on the web site of the provider. Those laboratories that had previously expressed interest in receiving information on the next PT were informed by email. Instructions for participants were part of the PT programme and were also distributed along with the test item. The sample remains property of the participant once the PT has been concluded.

4.2 Conditions for PT participation

By agreeing to participate in the PT, the participants committed to deliver within the designated period five parallel results of analyses, performed under the repeatability conditions (i.e. performed with the exact same equipment in an immediate and uninterrupted sequence). According to the requirements of the norm ČSN EN ISO/IEC 17043:2010 every measurement for the PT should be performed as a routine measurement that is under the same conditions and procedures as are usual in the everyday operation of the laboratory. The assessment method and (alternatively) the category and type of equipment are given by the participant in the PT protocol which was publicly accessible during the PT period at the web site of the provider www.spl-labmat.cz.

Based on the experience of the previous years, all the results submitted by participants, regardless of the method and equipment used, were included in the statistical data set. For evaluation, outlier exclusion was employed or alternatively robust statistics for elimination of the influence of outliers on the reference value and corresponding uncertainty.

Once the PT has been completed, the participants are provided:

Final report on the evaluation incl. evaluation of individual analytes.

Certificate of participation on the PT including two annexes.

Certificate of chemical analysis for new reference material

5. Preparation and homogeneity of the test items

Details concerning the preparation of the test items and measurements of homogeneity for this PT are presented in the **table 1 – general information on the PT**.

For the evaluation of homogeneity, we have employed our own programme using the statistical method ANOVA along with calculation of the standard deviation s from all assessments and their comparison to the usual values according to the norms or previous PTs. As the criterion of sufficient

homogeneity for the purpose of the PT, the condition to be met is $s < 0,5 s_N$, where s is the standard deviation in the measurement of homogeneity and s_N is the standard deviation according to the norm. Where no valid norm is available, an older norm with expired validity or a norm used in another country can be consulted, or comparison with values from previous PTs for similar materials. In case the $s < 0,5 s_N$ criterion is not met for some of the assessed parameters, non-homogeneity contribution can be taken into account by increasing s_{PT} and s_N for z -scoring assessment, in the following manner:

$$s_{PT}^* = \sqrt{s_{PT}^2 + s^2}$$

$$s_N^* = \sqrt{s_N^2 + s^2}$$

6. Statistic evaluation and performance standards

6.1 Reference value and related uncertainty

The statistical methods employed were used according to the norms ISO 13528:2005, ČSN ISO 5725-2:1997 a ČSN ISO 2602:1993.

Mean value of five results submitted by a single contributor is the **laboratory mean x** , which is equivalent to the arithmetic mean from five measurements and which represents the result of the laboratory for individual elements. The value of the measurement **uncertainty u** (repeatability), calculated from five assessments of a single laboratory, is also given.

This laboratory mean is given in bold on the pages with evaluation results for individual elements and it is used for subsequent statistical evaluation of laboratory results – that is statistical data sets for individual elements. Uncertainty u is given in the column on the right along with the laboratory mean x .

On the basis of this data set, the reference value is assessed and also the corresponding uncertainty. Also, if need be, Grubbs test according to the ČSN ISO 5725-2 is used to eliminate outlying results. Given the usual character of results in the provider's PT, in great majority of cases **consensual estimate of the reference value X_{PT}** is used. This can be calculated according to several statistical methods according to the algorithm given below. In this case the reference value on the page is marked $\hat{X} = X_{PT}$.

Where the provider considers it appropriate, in unique cases the reference value can be established on the basis of the results from selected laboratories with a long history of reliable results, where the probability of correct determination is higher. In these cases reference value in the table is marked as $\hat{X} = X_{Ref}$.

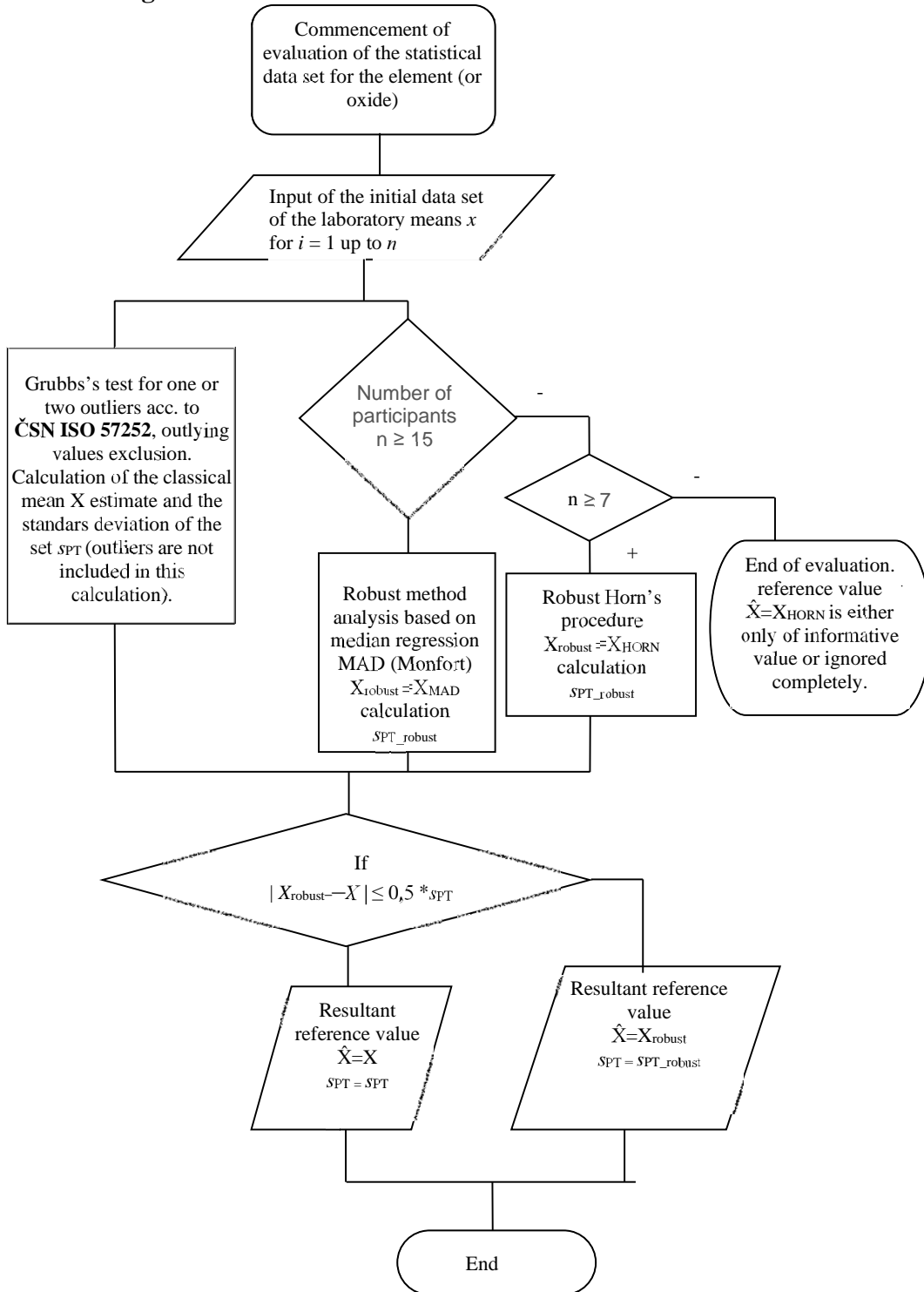
Basic statistical terms used

n	number of laboratories
p_i	number of assessments in i -th laboratory
y_{ik}	result of k -th assessment in the i -th laboratory
$i \in \{1, \dots, n\}$	laboratory index
$k \in \{1, \dots, p_i\}$	assessment index in the i -th laboratory
$x_i = \bar{y} = \frac{1}{n_i} \sum_{k=1}^{p_i} y_{ik}$	mean value of assessment in th i -th laboratory
$\bar{y} = \bar{x} = \frac{1}{n} \sum_{i=1}^n x_i$	mean value of evaluation from all laboratories
$s_i^2 = \frac{1}{p_i-1} \sum_{k=1}^{p_i} (y_{ik} - \bar{y}_i)^2$	variance in i -th laboratory
$s_{PT}^2 = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2$	value variance from all laboratories
$s_i = \sqrt{\frac{1}{p_i-1} \sum_{k=1}^{p_i} (y_{ik} - \bar{y}_i)^2}$	selected standard deviation of individual laboratory results
$s_{PT} = \sqrt{\frac{1}{p-1} \sum_{i=1}^p (x_i - \bar{x})^2}$	selected standard deviation of the data set from all participating laboratories in PT
$u_i = \pm \frac{t_{5;0,05}}{\sqrt{5}} \cdot s_i$	determination uncertainty (repeatability)
$U = \pm \frac{t_{5;0,05}}{\sqrt{n}} \cdot s_{PT}$	reference value uncertainty

Reference to the statistical methods used for the assessment of the reference value and its uncertainty

- **Arithmetic mean for elimination of outlying values by the Grubbs' test** according to ČSN ISO 5725-2.
- Robust method analysis based on median regression **MAD** (Montfort, M.A.J.von, Commun. Soil. Sci. Plant. Anal. 27, 463-468 (1996). This method is employed whenever the difference between AVG a MAD is above $0,5s_{PT}$ and at the same time, the number of laboratory means submitted is above 15.
- **Horn's procedures** (J. Horn, J. Am. Stat. Assoc., Volume 78, Page 930 (1983). Consensual reference value, robust method suitable for a smaller number of accepted laboratory means. It is being employed under the same conditions as the MAD, only for a lower number of accepted laboratory means, between 8 and 14. Whenever the number of laboratories is equal to or below 7 reference value is not assessed, or alternatively only as an informative value.

Evaluation algorithm:



6.2 Performance evaluation

z-scoring is done both for **subjective** Z_{PT} , i.e. calculated from the participants' data set – deviation s_{PT}

$$Z_{PT} = \frac{x - X}{s_{PT}}$$

and **objective** Z_N , based on the deviation given above derived from the norm s_N (if available), where

$$Z_N = \frac{x - X}{s_N}$$

If the s_N deviation is not available, subjective z-scoring Z_{PT} is used to assess the performance of the laboratory.

If the s_N deviation is available, the objective z-scoring Z_N is used to evaluate the performance and the subjective z-score Z_{PT} has only informative value. In a very limited number of cases, where the variability of laboratory means was larger, the subjective z-scoring was applied as criterion for individual elements.

Performance value of $|Z_{PT}| \leq 2$ is considered **„satisfactory“**

Performance value of $2 < |Z_{PT}| \leq 3$ is considered **„problematic“**

Performance value of $|Z_{PT}| > 3$ is considered **„unsuitable“**.

Problematic performance value calls for attention, **unsuitable** performance calls for correction.

7. PT evaluation results summary

Table 2

Element	X [%wt.]	U [%wt.]	s_{PT} [%wt.]	s_N [%wt.]	No of laboratories in the data set	Overall No of laboratories	No of laboratories where the criteria were exceeded
Mn	80.70	0.45	0.71		12	13	2
C	0.921	0.009	0.013		11	12	1
Si	0.422	0.084	0.125		11	11	0
P	0.204	0.004	0.003		9	11	2
S	0.0053	0.0011	0.0017		11	11	1

X – reference value

U – reference value uncertainty

s_{PT} – data set standard deviation

s_N – standard deviation according to the norm

8. Conclusion

Names of participating laboratories are stated in the Certificate of chemical analysis. Reference material produced as the result of PT 32/9A is named **S-4A**.

PT 32/9A - Mn

Results, statistical parameters and scoring

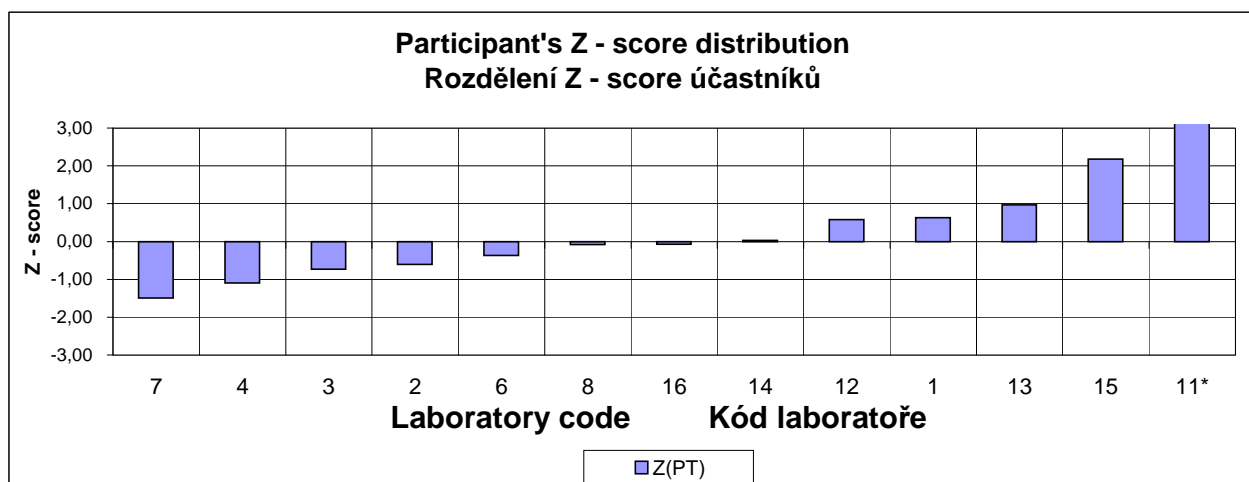
Výsledky, statistické parametry a scoring

Code	Method	Individual results % [wt. %], Jednotlivé výsledky [hm. %]					x [%]	u [%]	Z _{PT}
Kód	Metoda	1.	2.	3.	4.	5.	average	repeatability	Z-score _{PT}
5		-							
9		-							
10		-							
7	Titrimetric	79,67	79,68	79,64	79,53	79,70	79,64	0,08	-1,49
4	XRF	79,82	79,79	80,12	79,91	79,95	79,92	0,16	-1,10
3	XRF	80,12	80,13	80,23	80,20	80,24	80,18	0,07	-0,73
2	Titrimetric	80,12	80,29	80,46	79,89	80,59	80,27	0,34	-0,61
6	XRF	80,37	80,49	80,41	80,44	80,48	80,44	0,06	-0,37
8	ICP	81,11	80,81	80,60	80,40	80,30	80,64	0,40	-0,08
16	Titrimetric	80,74	80,52	80,52	80,74	80,74	80,65	0,15	-0,07
14	XRF	80,76	80,98	80,77	80,61	80,50	80,72	0,23	0,03
12	XRF	81,12	81,09	81,08	80,99	81,27	81,11	0,13	0,58
1	XRF	81,06	81,17	81,25	81,12	81,16	81,15	0,09	0,63
13	XRF	81,43	81,31	81,45	81,42	81,34	81,39	0,08	0,97
15	XRF	82,48	82,13	82,49	82,17	81,98	82,25	0,28	2,18
11*	ICP	83,99	84,23	84,42	85,41	84,55	84,52	0,67	5,38

* - result excluded as outlier

* - výsledek vyloučen jako odlehlý

n	$\bar{X} = X_{PT}$ [%]	S _{PT} [%]	S _N [%]	U [%]
12	80,70	0,71		0,45



PT 32/9A - C

Results, statistical parameters and scoring

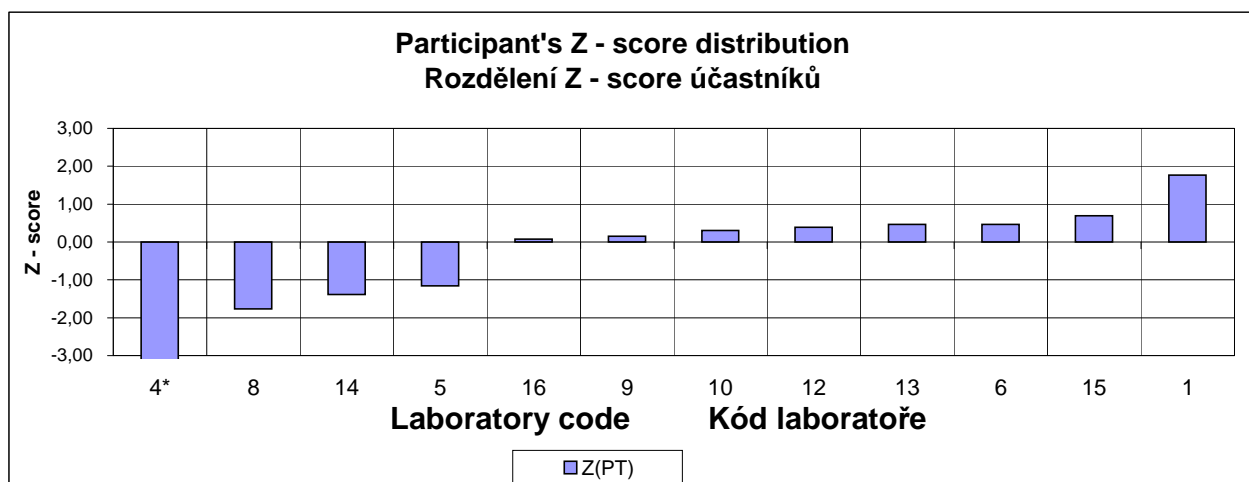
Výsledky, statistické parametry a scoring

Code	Method	Individual results % [wt. %], Jednotlivé výsledky [hm. %]					x [%]	u [%]	Z _{PT}
Kód	Metoda	1.	2.	3.	4.	5.	average	repeatability	Z-score _{PT}
2		-							
3		-							
7		-							
11		-							
4*	IR	0,808	0,820	0,826	0,830	0,823	0,821	0,010	-7,69
8	IR	0,897	0,899	0,898	0,901	0,895	0,898	0,003	-1,77
14	IR	0,903	0,901	0,907	0,903	0,902	0,903	0,003	-1,38
5	IR	0,906	0,904	0,909	0,907	0,906	0,906	0,002	-1,15
16	IR	0,922	0,923	0,919	0,925	0,922	0,922	0,003	0,08
9	IR	0,915	0,919	0,930	0,930	0,922	0,923	0,008	0,15
10	IR	0,925	0,925	0,925	0,924	0,927	0,925	0,001	0,31
12	IR	0,923	0,918	0,921	0,926	0,944	0,926	0,013	0,38
13	XRF	0,931	0,940	0,917	0,919	0,926	0,927	0,012	0,46
6	IR	0,928	0,926	0,924	0,926	0,929	0,927	0,002	0,46
15	IR	0,930	0,934	0,934	0,944	0,906	0,930	0,018	0,69
1	IR	0,930	0,960	0,960	0,930	0,940	0,944	0,019	1,77

* - result excluded as outlier

* - výsledek vyloučen jako odlehlý

n	$\bar{X} = X_{PT}$ [%]	S _{PT} [%]	S _N [%]	U [%]
11	0,921	0,013		0,009



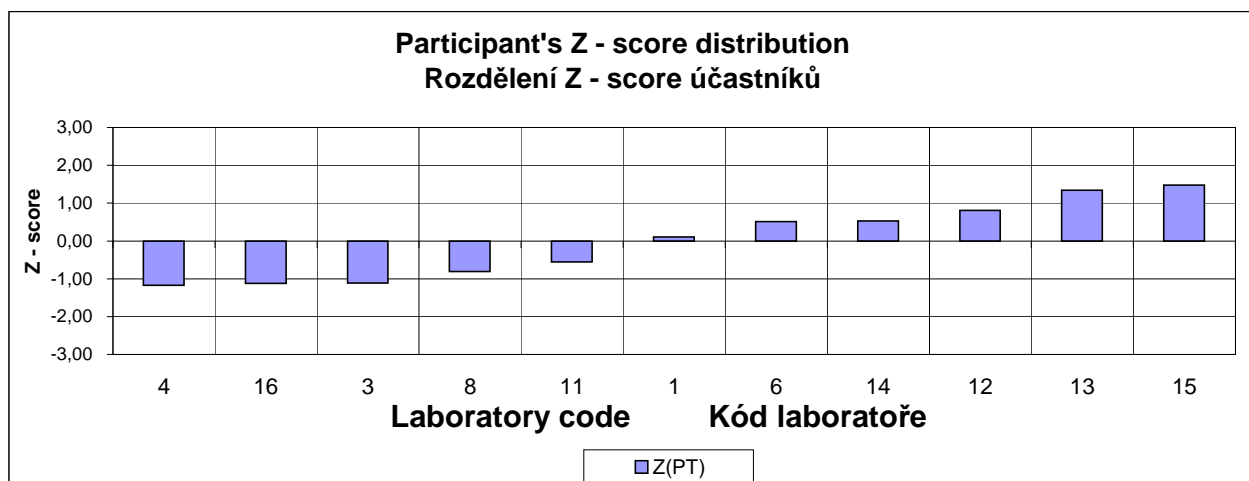
PT 32/9A - Si

Results, statistical parameters and scoring

Výsledky, statistické parametry a scoring

Code	Method	Individual results % [wt. %], Jednotlivé výsledky [hm. %]					x [%]	u [%]	Z _{PT}
Kód	Metoda	1.	2.	3.	4.	5.	average	repeatability	Z-score _{PT}
2		-							
5		-							
7		-							
9		-							
10		-							
4	XRF	0,298	0,277	0,247	0,269	0,287	0,276	0,024	-1,17
16	Gravimetric	0,280	0,290	0,280	0,280	0,280	0,282	0,006	-1,12
3	XRF	0,281	0,284	0,278	0,280	0,293	0,283	0,007	-1,11
8	Gravimetric	0,312	0,337	0,333	0,313	0,310	0,321	0,016	-0,81
11	ICP	0,364	0,359	0,366	0,336	0,338	0,353	0,018	-0,55
1	XRF	0,436	0,413	0,427	0,459	0,438	0,435	0,021	0,10
6	XRF	0,496	0,492	0,493	0,479	0,472	0,486	0,013	0,51
14	XRF	0,440	0,440	0,510	0,530	0,520	0,488	0,055	0,53
12	XRF	0,516	0,519	0,527	0,526	0,527	0,523	0,006	0,81
13	XRF	0,574	0,604	0,578	0,608	0,588	0,590	0,019	1,34
15	XRF	0,597	0,614	0,596	0,613	0,616	0,607	0,012	1,48

n	$\bar{X} = X_{PT}$ [%]	S _{PT} [%]	S _N [%]	U [%]
11	0,422	0,125		0,084



PT 32/9A - P

Results, statistical parameters and scoring

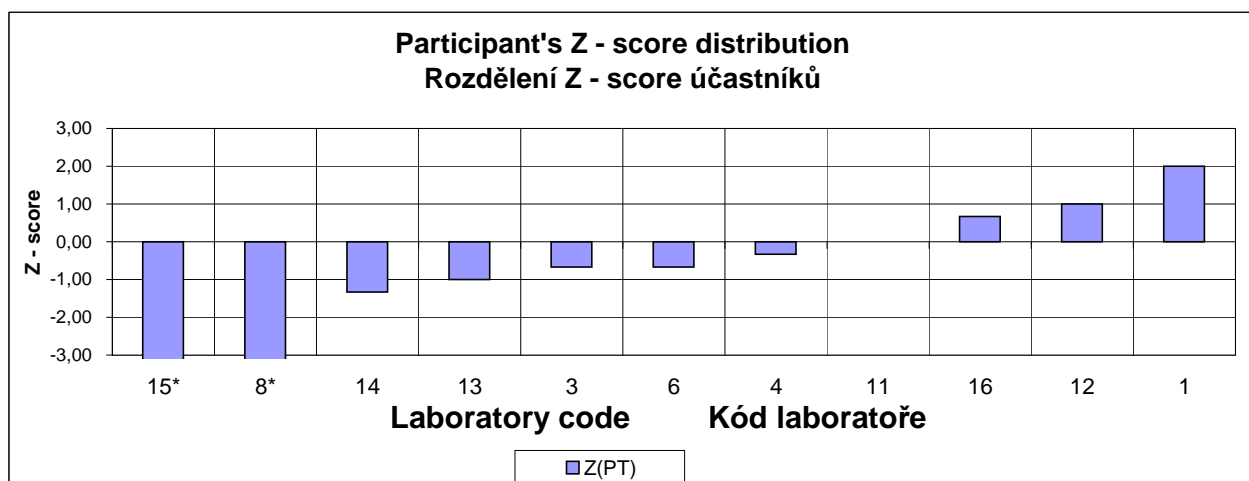
Výsledky, statistické parametry a scoring

Code	Method	Individual results % [wt. %], Jednotlivé výsledky [hm. %]					x [%]	u [%]	Z _{PT}
Kód	Metoda	1.	2.	3.	4.	5.	average	repeatability	Z-score _{PT}
2		-							
5		-							
7		-							
9		-							
10		-							
15*	XRF	0,185	0,185	0,185	0,185	0,185	0,185	0,000	-6,33
8*	ICP	0,186	0,192	0,188	0,188	0,186	0,188	0,003	-5,33
14	XRF	0,198	0,205	0,202	0,199	0,198	0,200	0,004	-1,33
13	XRF	0,201	0,201	0,202	0,200	0,201	0,201	0,001	-1,00
3	XRF	0,199	0,203	0,204	0,202	0,204	0,202	0,003	-0,67
6	XRF	0,199	0,200	0,202	0,203	0,205	0,202	0,003	-0,67
4	XRF	0,203	0,208	0,203	0,199	0,202	0,203	0,004	-0,33
11	ICP	0,205	0,200	0,200	0,206	0,208	0,204	0,004	0,00
16	Titrimetric	0,200	0,210	0,200	0,210	0,210	0,206	0,007	0,67
12	XRF	0,203	0,207	0,205	0,209	0,209	0,207	0,003	1,00
1	XRF	0,202	0,204	0,210	0,216	0,218	0,210	0,009	2,00

* - result excluded as outlier

* - výsledek vyloučen jako odlehlý

n	$\bar{X} = X_{PT}$ [%]	S _{PT} [%]	S _N [%]	U [%]
9	0,204	0,003		0,004



PT 32/9A - S

Results, statistical parameters and scoring

Výsledky, statistické parametry a scoring

Code	Method	Individual results % [wt. %], Jednotlivé výsledky [hm. %]					x [%]	u [%]	Z _{PT}
Kód	Metoda	1.	2.	3.	4.	5.	average	repeatability	Z-score _{PT}
2		-							
3		-							
4		-							
7		-							
11		-							
8	IR	0,0015	0,0020	0,0016	0,0023	0,0017	0,0018	0,0004	-2,06
13	XRF	0,0030	0,0040	0,0030	0,0030	0,0030	0,0032	0,0006	-1,24
5	IR	0,0046	0,0044	0,0046	0,0044	0,0043	0,0045	0,0002	-0,47
1	IR	0,0050	0,0040	0,0050	0,0050	0,0050	0,0048	0,0006	-0,29
12	XRF	0,0052	0,0048	0,0048	0,0049	0,0051	0,0050	0,0002	-0,18
14	IR	0,0051	0,0054	0,0048	0,0055	0,0053	0,0052	0,0003	-0,06
15	IR	0,0064	0,0065	0,0061	0,0061	0,0064	0,0063	0,0002	0,59
6	IR	0,0062	0,0062	0,0064	0,0065	0,0067	0,0064	0,0003	0,65
9	IR	0,0078	0,0061	0,0069	0,0058	0,0074	0,0068	0,0011	0,88
10	IR	0,0064	0,0079	0,0073	0,0069	0,0065	0,0070	0,0008	1,00
16	IR	0,0072	0,0078	0,0082	0,0070	0,0078	0,0076	0,0006	1,35

n	$\bar{X} = X_{PT}$ [%]	S _{PT} [%]	S _N [%]	U [%]
11	0,0053	0,0017		0,0011

