METROLOGY SERVICE

Director
Metrology service Ltd.

Bozhko Nataliia
November 11th 2020

PROFICIENCY TESTING PT.UA.2.10.2019

ANIMAL FEEDING STUFFS (MICROELEMENTS)

PROFICIENCY TESTING REPORT

ROUND 2 OCTOBER 2020

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2. SUMMARY

2.1. The purpose of proficiency testing in animal feeding stuff elements testing is to determine the characteristics of the operation (as described in ISO/IEC 17043:2010[1]) and improve the reliability of test results.

2.2. This proficiency testing involves the use of inter-laboratory comparisons to confirm the performance of individual laboratories' abilities and/or identify areas of improvement. Current PT scheme is registered in the EPTIS database.

2.3. This is the final report on the PT.UA.2.10.2019 ROUND 2 held in October 2020. This report is issued according to ISO/IEC 17043[1] and PT.UA.2.10.2019 ROUND 2 Programme. The report is issued in two languages – Ukrainian and English. English should be considered as the basic language of the report. Both versions of this report can be found at: http://www.metrologyservice.com.ua

2.4. A total of 10 participants have reported. Their results are presented in the next clauses.

2.5. Technical experts list and/or subcontractors for this round can be provided to the Participant by request.

2.6. Any calculations, formulas, raw and intermediate data used in this round can be provided to the Participant by request, except confidential information about other participants and information that may contain commercial secret.

2.7. Clause 9 of this report stated for information purposes only. Provider did not assess any results based on this information.

3. GENERAL PROTOCOL FOR PROFECIENCY TESTING

3.1. MANAGEMENT SYSTEM.

3.1.1. The functioning management system of Metrology service Ltd. (further - Provider) complies with ISO/IEC 17043[1] requirements and covers all aspects of proficiency testing (further - PT) for all proficiency tests.

3.2. SAMPLES PREPARATION, HOMOGENITY AND STABILITY

3.2.1. Provider has used a validated procedure and appropriate technical experts and contractors for the samples' selection, production, homogenization and division designs that is proved to be satisfactory for the purposes of PT programme PT.UA.2.10.2019 ROUND 2. Details of test material preparation and homogenization are not published in the report, though can be provided to the Participant by request. Tests, required to prove (validate) homogeneity and stability of samples were performed by competent contracting laboratories according to [2-7]. These results with statistics are published in the report.

3.2.2. Participants may contact the Provider to request details of test material selection, preparation, homogenization and division of those test material samples, for which they tested in PT. Such information can be provided to the Participant in confidence and only if it cannot compromise other Participants and/or is not a commercial secret.

3.3. DISPATCH AND RECEIPT OF SAMPLES

3.3.1. Samples of test material – **homogenized animal feeding stuff** were dispatched 19.10.2020 according to schedule of proficiency testing programme PT.UA.2.10.2019 ROUND 2.

3.3.2. Each produced and identified sample was hermetically sealed.

3.3.3. A total of 10 participants from different regions of Ukraine received one sample. Results were returned from 10 participants.

3.4. FOLLOW-UP SERVICES

3.4.1. If a participant wishes to obtain advice/consultation on any aspect of their performance, one should contact the Provider. Provider can (with agreement with Participant) pass on the Participant's inquiry to a technical expert and/or contracting laboratory.

3.4.2. Surplus samples from this round are available for sale as certified reference materials (CRM) with the certified values and uncertainties. Please email Provider for details.

3.5. PERFORMANCE ASSESMENT

3.5.1. Provider expressed Participant's results as traditional z-scores according to [1].

3.5.2. The assigned value for each analyte was calculated as the robust mean of the trial data using Huber H15 method [2,3]

3.5.3 The target standard deviation for each analyte was chosen from either the appropriate form of the Horwitz equation, method trial standard deviation (if stated in the method from inter-laboratory comparisons), standard deviation from the previous trials (PT rounds, see clause 3.5.6), or the robust trial standard deviation, after the removal of outliers. The choice was made using current industry practices used in other collaborative trials and proficiency testing schemes.

3.5.4. z-Scores were deemed satisfactory if $|z| \leq 2$. z-Scores were deemed questionable if $2 < |z| \leq 3$(marked yellow in tables). If $|z| \geq 3$, the results were considered to be unsatisfactory (marked red in tables). The calculations were made according to [1,3,5].

3.5.5. Only 1.54% (1 result) of all results in this round are considered to be unsatisfactory. In Round 1, there were 11,76% (6 results) unsatisfactory results.

4. HOMOGENITY AND STABILITY ASSESMENT

4.1. Samples were assessed for homogeneity after blending and packing by selecting seven samples of material at random from all those produced. These samples were tested in duplicate under repeatability conditions as only 22 samples were produced according to [7].

4.2. Statistical analysis of the resulting data for homogeneity and stability was carried out using the industry standard Cochran's 'C' test and analytical variance test for 'sufficient homogeneity' according to [3,4].

4.3. Produced samples were found to be sufficiently homogeneous and stable for every analyte according to programme, except for those that can be considered equivalent or homogeneity can be assumed from other analyte homogeneity.

4.4. Cobalt (Co), mg/kg

Cobalt (Co), mg/kg

Дослідження гомогенності/Homogenity test

Аналіз викидів за тестом Кохрана(C -тест)/Cohran's C test for outliers

Номер зразку/ Sample number	Результат/ Result A	Результат/ Result B	Average	SD²	
1	0,24	0,23	0,24	0,0000	0,00
2	0,23	0,25	0,24	0,0002	0,00
3	0,23	0,26	0,25	0,0005	0,00
4	0,25	0,24	0,25	0,0001	0,00
5	0,25	0,24	0,25	0,0001	0,00
6	0,26	0,27	0,27	0,0001	0,00
7	0,20	0,19	0,20	0,0001	0,00

Mean	0,239	Worst pair	0,0005
Max	0,27	SUM of SD²	0,0009
Min	0,19	C	0,5000
		Ccr, 5%	0,7271
		Ccr, 1%	0,8376
		Conclusion	
		5%	PASS
		1%	PASS

Аналіз на 'достатню однорідність'/Test for 'sufficient homogenity'

Номер зразку /Sample number	Результат/ Result A	Результат/ Result B	SUM	Difference²
1	0,24	0,23	0,47	0,0001
2	0,23	0,25	0,48	0,0004
3	0,23	0,26	0,49	0,0009
4	0,25	0,24	0,49	0,0001
5	0,25	0,24	0,49	0,0001
6	0,26	0,27	0,53	0,0001
7	0,20	0,19	0,39	0,0001
				0,0018

Mean	0,239		
Max	0,27		
Min	0,19		
Analytical variance S²an	0,0001	SD	0,0221
Sanal	0,0113	RSDR	9,2796
Ssums	0,0018		
MSb	0,0009		
Between sample variance S²sam	0,0004		

Remarks

1. Cohran's C test is described in ISO 5727-2 and FAPAS protocol, sixth edition, 2002
2. Test for 'sufficient homogenity' is performed according to FAPAS protocol, sixth edition, 2002

Source of σp value to use		
Use(write '1')	Source	σp
	C>13.8%, HORWITZ	4,8844
1	120ppb<C<13.8%, HORWITZ	0,0473
	C<120 ppb	0,052486
MASS NEGATIVE POWER FOR HORWITZ EQUATION(%=2, ppb=9,ppm=6)		6
	SD	0,0213
	Trial SD	278,5880
	Target SD chosen	0,0473
	σ²all	0,000202
	Replicates	7
	F1	2,1
	F2	1,43
	Critical value	0,0006
	Between sample variance S²sam	0,0004
	Sufficient homogenity test	PASS

4.6. Data for all analytes

	Calcium (Ca), mg/kg	Cobalt (Co), mg/kg	Cuprum (Cu), mg/kg	Iron (Fe), mg/kg	Manganese (Mn), mg/kg	Selenium (Se), mg/kg	Sodium (Na), mg/kg	Zinc (Zn), mg/kg
Homogenity and stability (Гомогенність та стабільність)								
Cohran's 'C' test (С-тест "Кохрана")								
Crtitical value (5%,7pairs)=0,7271	0,4968	0,5000	0,4241	0,5664	0,3350	0,5515	0,6685	0,3568
Mean Result	7562,7143	0,2386	22,1357	191,2857	77,3643	0,7057	1446,7857	132,5000
Conclusion (Висновок)	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Analytical variance test (тест аналітичної дисперсії)								
S^2anal	127845,8571	0,0001	6,6850	40,8571	55,2721	0,0029	25970,0714	16,2143
Sanal	357,5554	0,0113	2,5855	6,3920	7,4345	0,0540	161,1523	4,0267
S^2sample	82707,8929	0,0004	1,1256	45,9762	0	0,0024	12680,9524	21,3929
σ_p	315,4763	0,0473	3,3440	21,5800	6,4320	0,2190	102,7390	17,2500
σ_p source	Horwitz	Horwitz	Trial SD	Trial SD	Horwitz	Trial SD	Trial SD	Trial SD
σ^2all	8957,2749	0,0002	1,0064	41,9127	3,7233	0,0043	949,9772	26,7806
Critical value	201629,8530	0,0006	11,6730	146,4423	86,8582	0,0132	39132,1542	79,4257
Conclusion (Висновок)	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS

5. DATA SUMMARY

	Calcium (Ca), mg/kg	Cobalt (Co), mg/kg	Cuprum (Cu), mg/kg	Iron (Fe), mg/kg	Manganese (Mn), mg/kg	Selenium (Se), mg/kg	Sodium (Na), mg/kg	Zinc (Zn), mg/kg
No of Results	9	7	10	10	8	3	8	10
No of Results |z|>3	0	1	0	0	0	0	0	0
No of Results |z|>3, %	0,000	14,286	0,000	0,000	0,000	0,000	0,000	0,000
Mean	7348,664	0,351	23,071	210,346	81,681	0,478	1684,937	137,767
Min	6505,000	0,230	17,890	164,000	65,640	0,330	1436,000	112,600
Max	7887,682	0,860	29,820	242,000	90,000	0,730	1833,250	164,000
SD	427,114	0,227	3,701	24,526	8,499	0,219	129,597	17,316
Median	7349,000	0,272	23,503	214,303	83,950	0,374	1711,351	135,165
Robust mean (assigned value)	7389,050	0,277	22,878	211,899	82,491	0,478	1698,483	137,727
Robust SD	347,048	0,045	3,344	21,580	6,913	0,219	102,739	17,250
SD from method (Tr.SD)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
SD from Horwitz eq.	309,311	0,054	2,285	15,138	6,792	0,085	88,709	10,499
Target SD	309,311	0,054	3,344	21,580	6,792	0,219	102,739	17,250
Source of target SD of PT	Horwitz	Horwitz	Trial SD	Trial SD	Horwitz	Trial SD	Trial SD	Trial SD

6. RAW DATA

Laboratory number	Calcium (Ca), mg/kg	Cobalt (Co), mg/kg	Cuprum (Cu), mg/kg	Iron (Fe), mg/kg	Manganese (Mn), mg/kg	Selenium (Se), mg/kg	Sodium (Na), mg/kg	Zinc (Zn), mg/kg
1			29,82	231,20				152,31
2	6505 мг/кг		24,7 мг/кг	164 мг/кг	89,5 мг/кг		1436 мг/кг	126,3 мг/кг
3	7425,00	0,24	23,10	229,00	86,40	0,37	1719,00	136,00
4	7295,78	0,23	26,35	206,25	90,00		1833,25	134,33
5	7023,80	0,30	17,89	206,72	72,56		1712,00	112,60
6	7349,00	0,32	25,10	227,00	85,00	0,33	1828,00	152,00
7	7195,71	0,86	20,04	190,40	65,64		1653,54	114,09
8	7854,00	0,24	21,20	185,00	82,90	0,73	1587,00	133,00
9	7602,00		18,60	242,00				164,00
10	7887,68	0,27	23,91	221,89	81,45		1710,70	153,04

7. Z SCORES

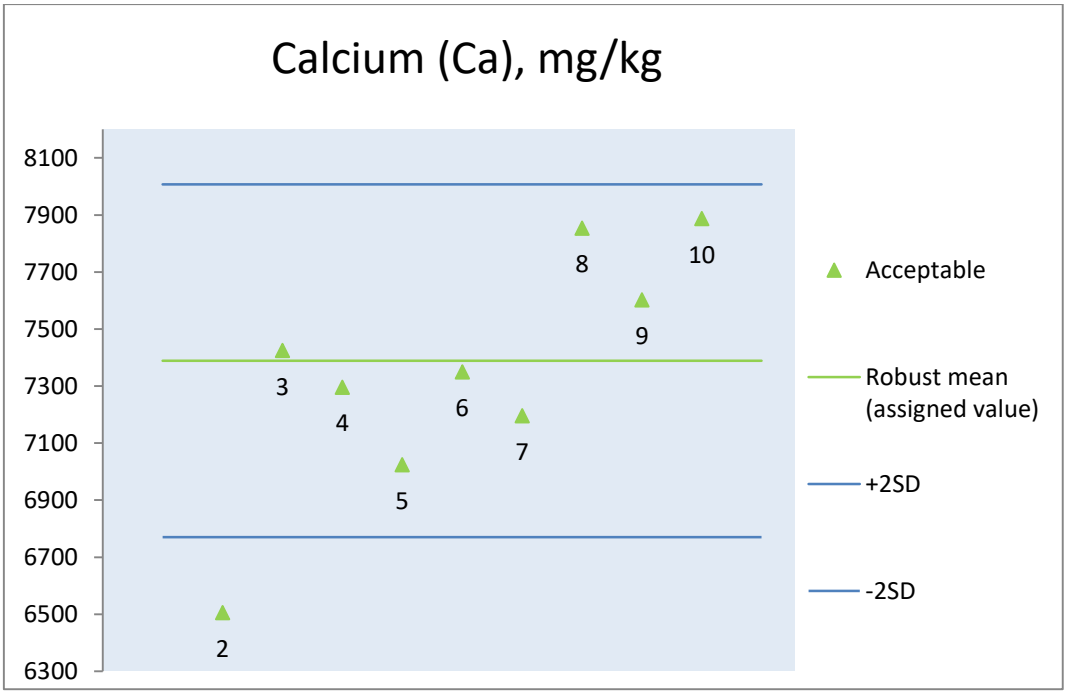
Laboratory number	Calcium (Ca), mg/kg	Cobalt (Co), mg/kg	Cuprum (Cu), mg/kg	Iron (Fe), mg/kg	Manganese (Mn), mg/kg	Selenium (Se), mg/kg	Sodium (Na), mg/kg	Zinc (Zn), mg/kg
1			2,08	0,89				0,85
2	-2,86		0,54	-2,22	1,03		-2,55	-0,66
3	0,12	-0,79	0,07	0,79	0,58	-0,47	0,20	-0,10
4	-0,30	-0,88	1,04	-0,26	1,11		1,31	-0,20
5	-1,18	0,40	-1,49	-0,24	-1,46		0,13	-1,46
6	-0,13	0,79	0,66	0,70	0,37	-0,67	1,26	0,83
7	-0,63	10,83	-0,85	-1,00	-2,48		-0,44	-1,37
8	1,50	-0,69	-0,50	-1,25	0,06	1,15	-1,09	-0,27
9	0,69		-1,28	1,39				1,52
10	1,61	-0,10	0,31	0,46	-0,15		0,12	0,89

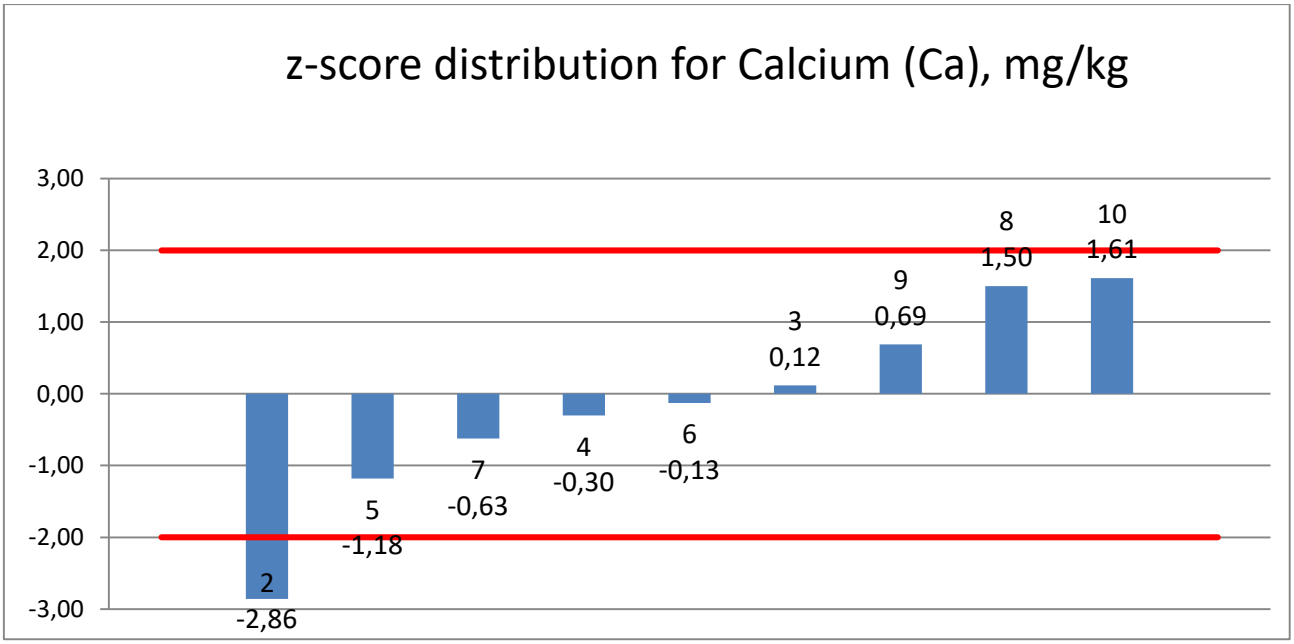
Remarks

1. Blank cell – results were reported as “not tested” by the Participants.
2. Results that are considered to be unsatisfactory are marked by red colored cell.
3. Results that are considered to be questionable are marked by yellow colored cell.
4. Results that are considered to be satisfactory are marked by green colored cell.

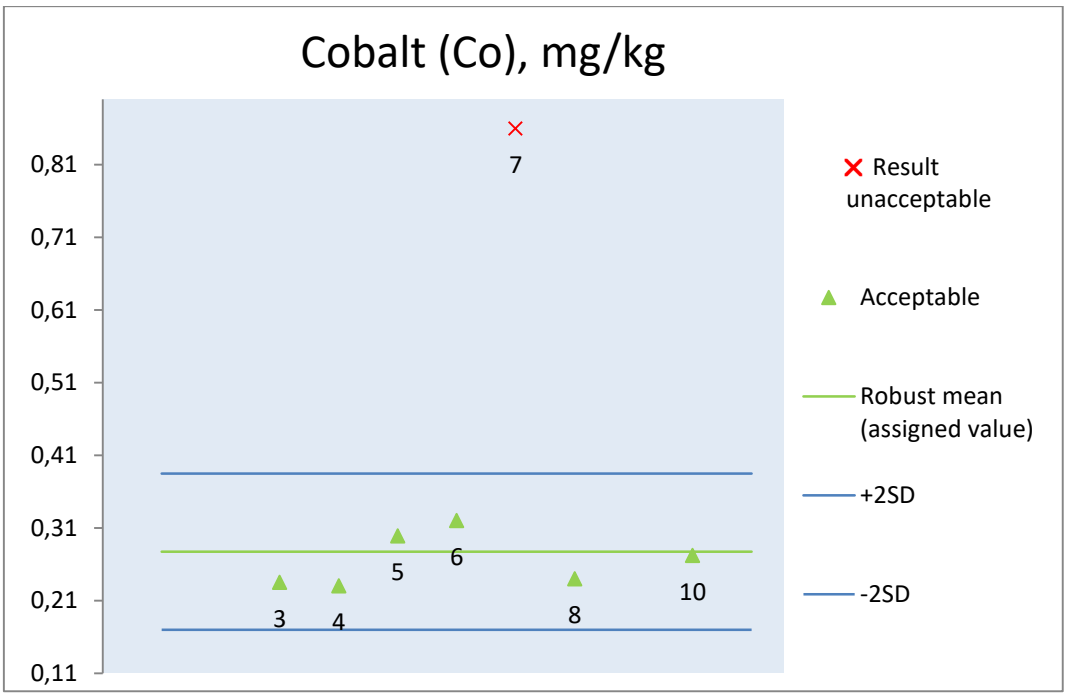
8. Z SCORE PLOTS AND RESULTS CHARTS.

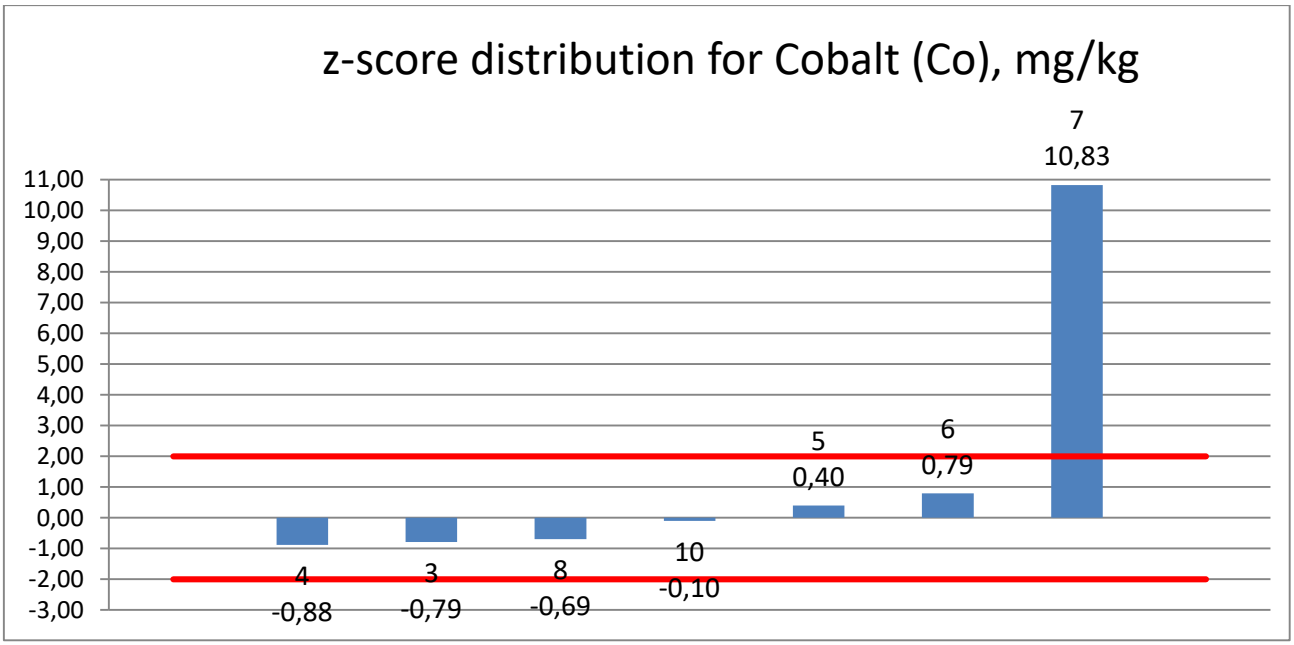
8.1. Calcium (Ca), mg/kg



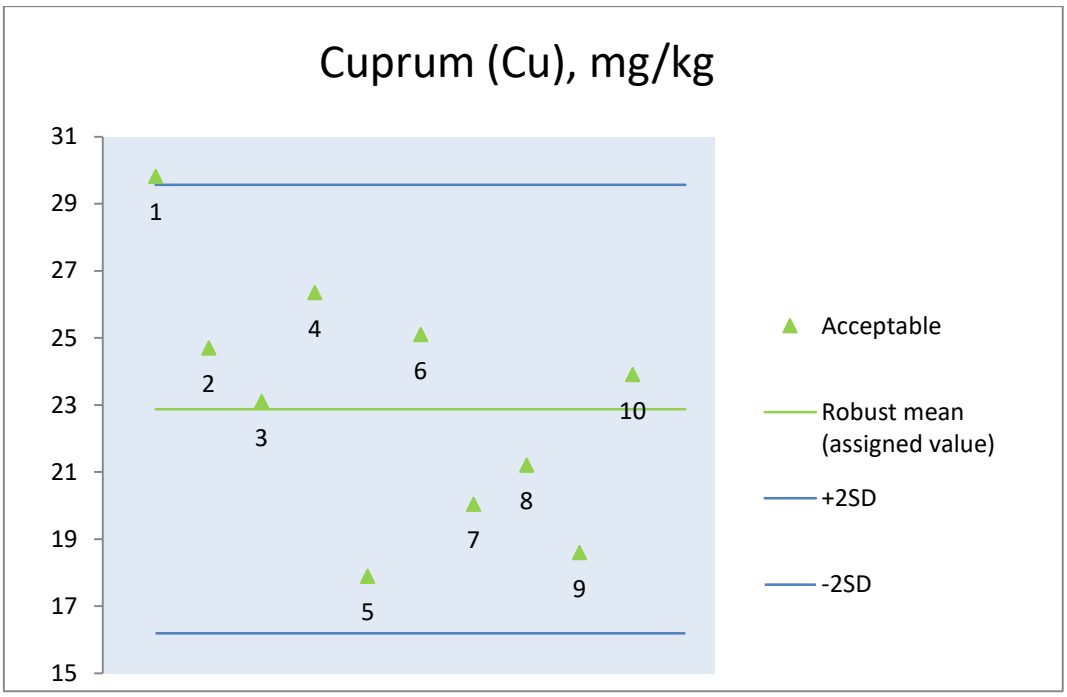


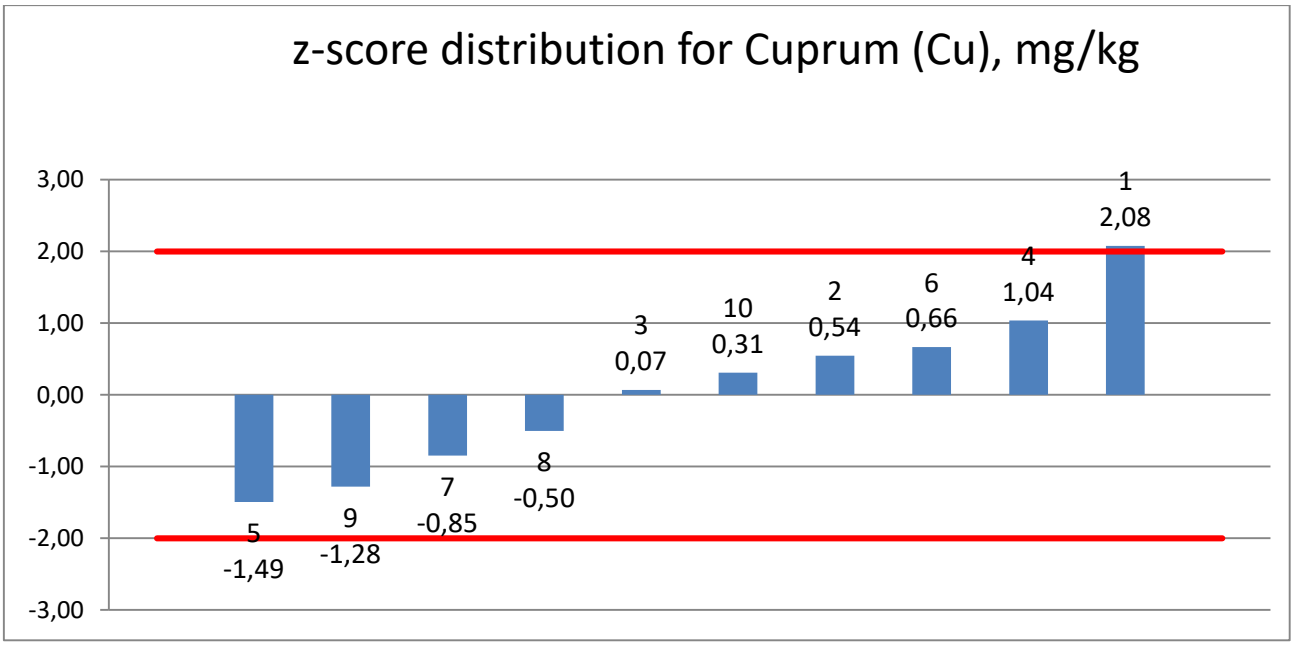
8.2. Cobalt (Co), mg/kg



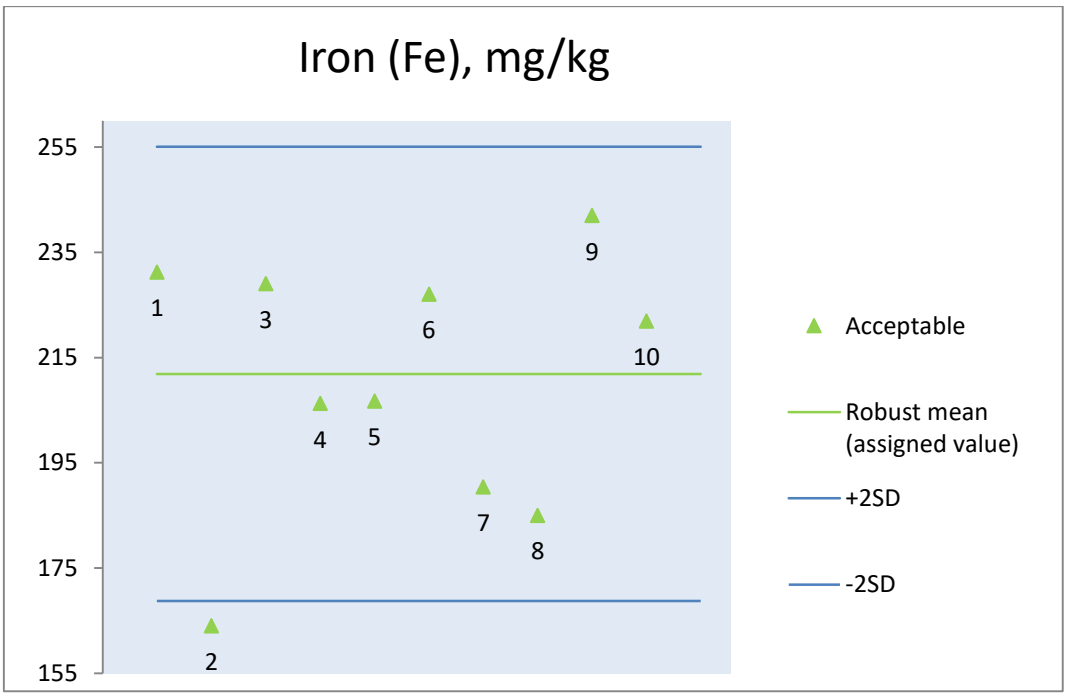


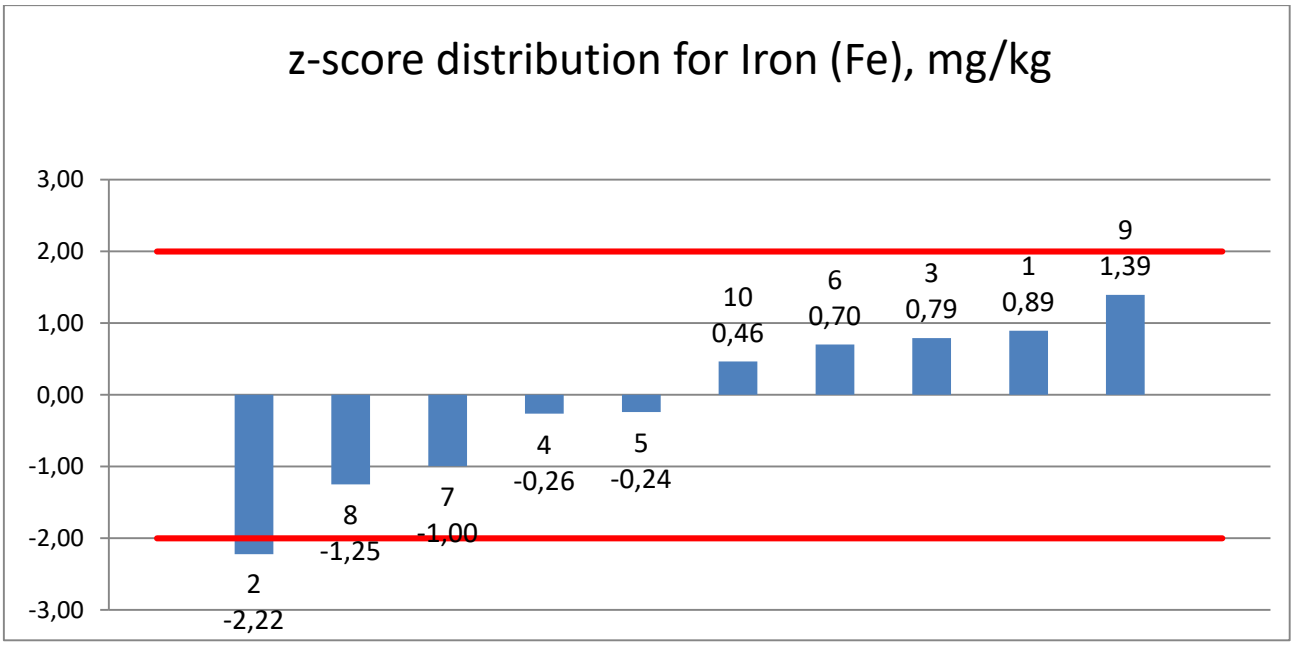
8.3. Cuprum (Cu), mg/kg



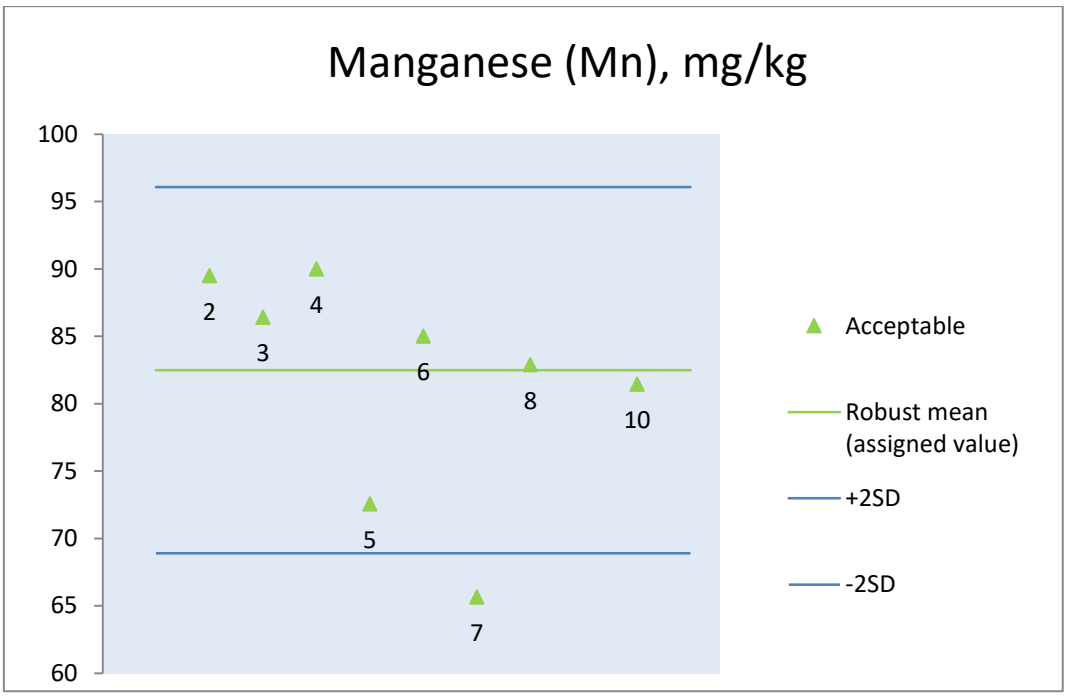


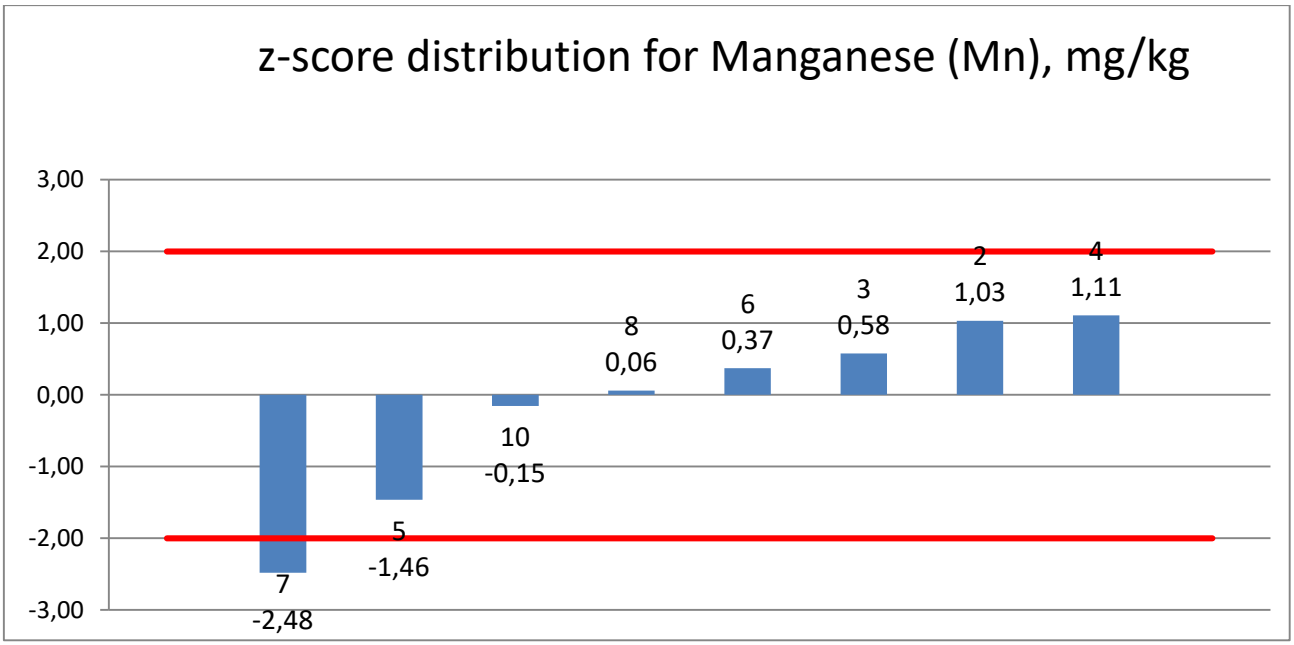
8.4. Iron (Fe), mg/kg



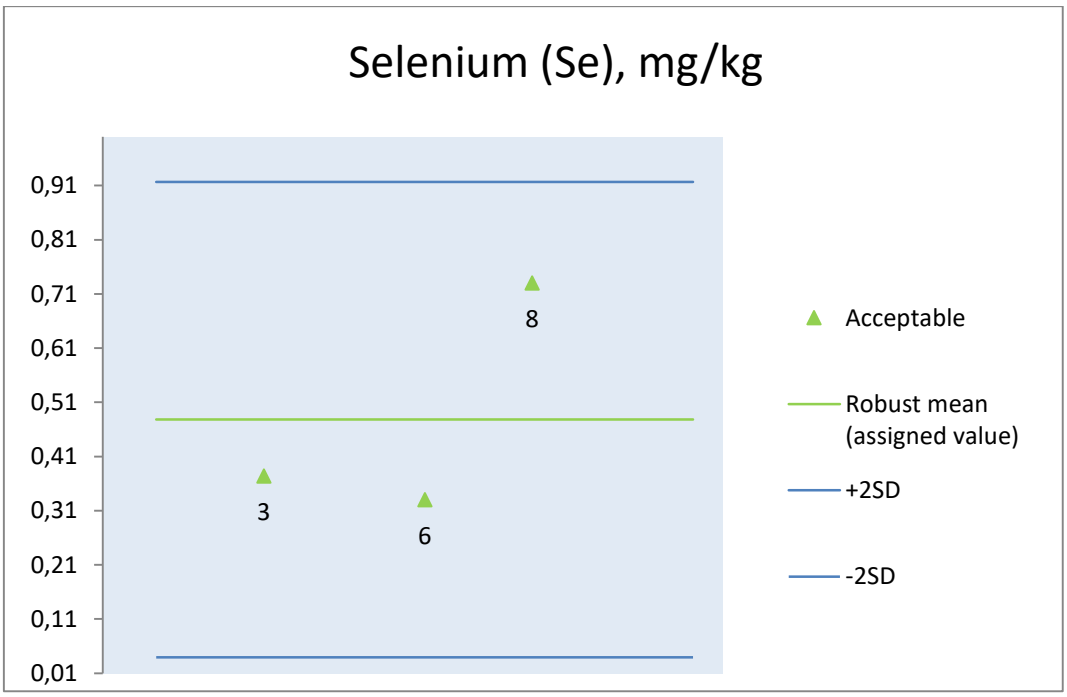


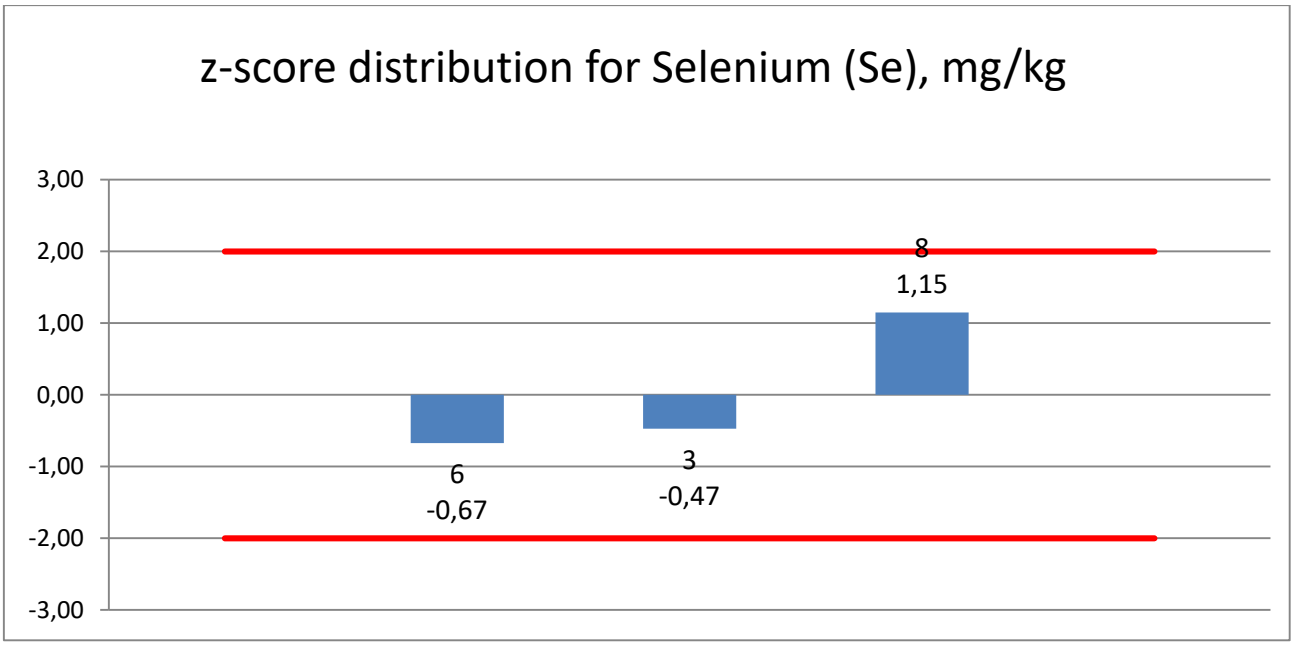
8.5. Manganese (Mn), mg/kg



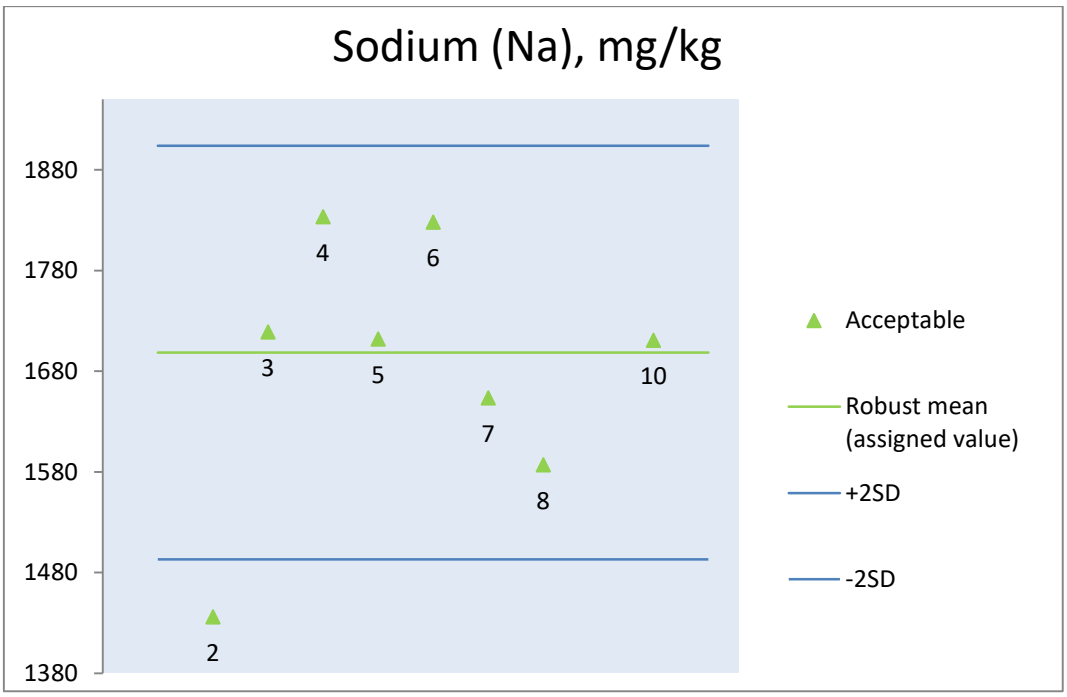


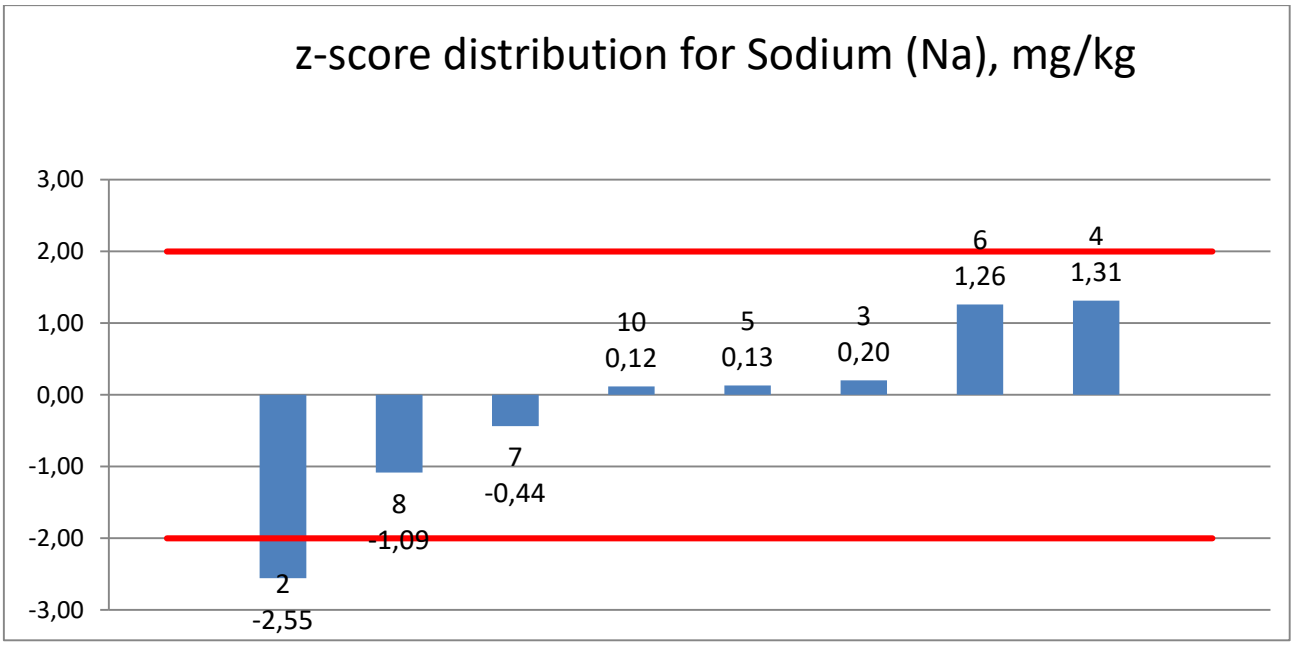
8.6. Selenium (Se), mg/kg



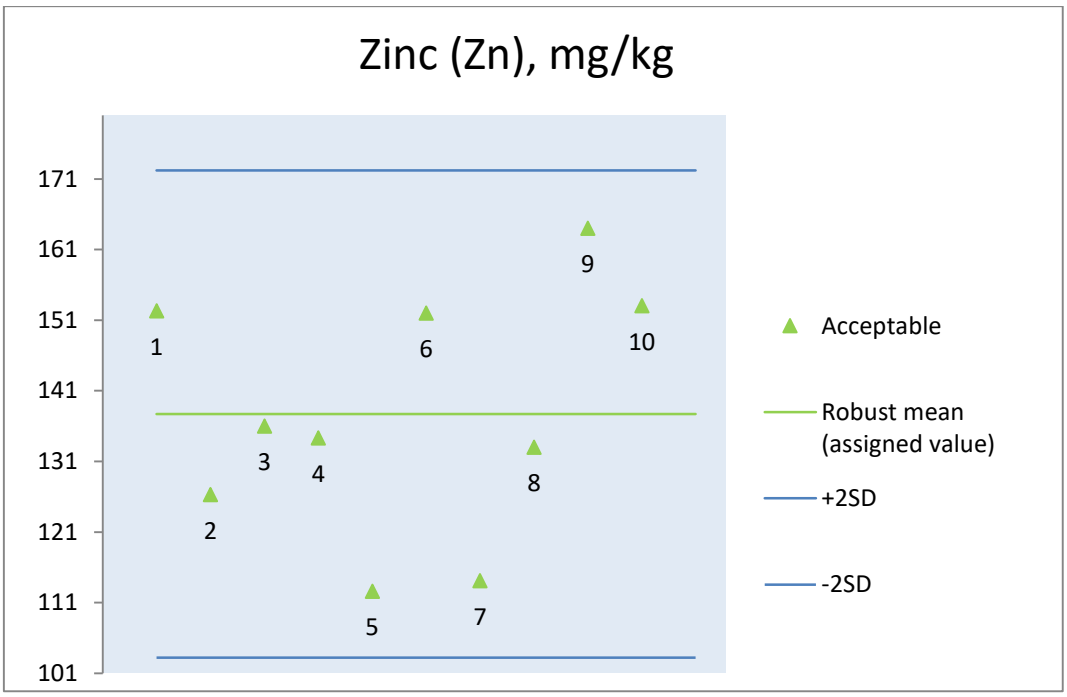


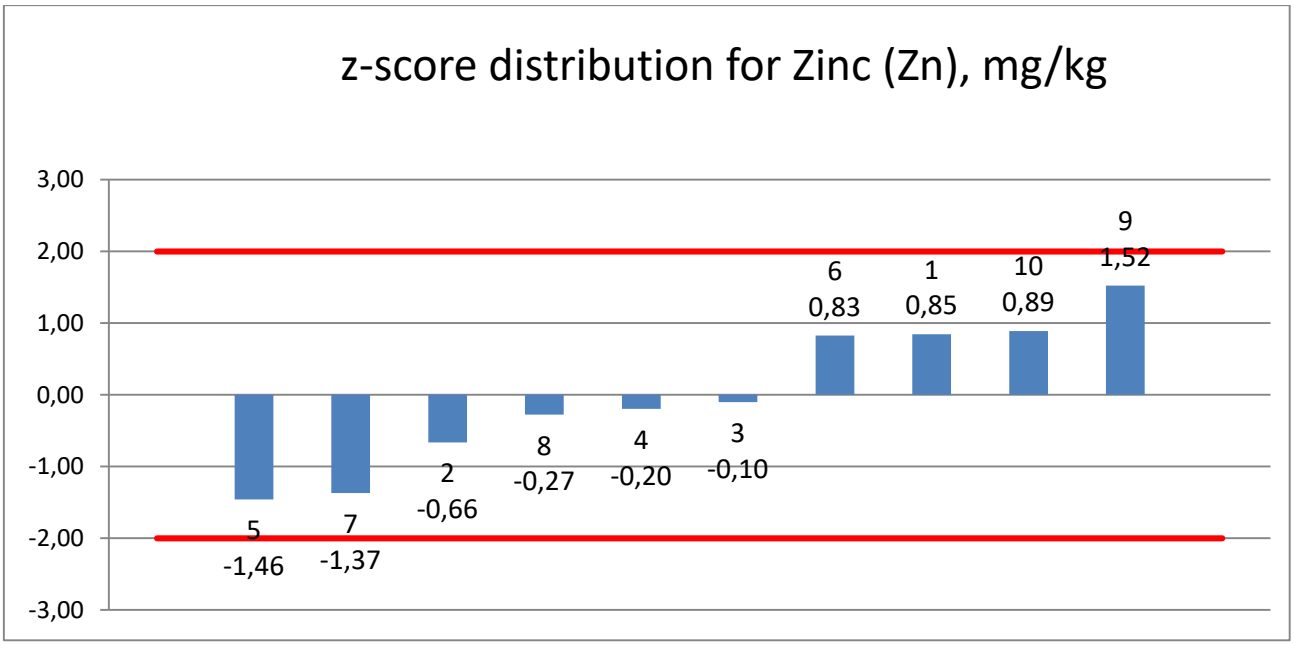
8.7. Sodium (Na), mg/kg





8.8. Zinc (Zn), mg/kg





9. REFERENCE INFORMATION

9.1. Methods

Laboratory number	Calcium (Ca), mg/kg	Cobalt (Co), mg/kg	Cuprum (Cu), mg/kg	Iron (Fe), mg/kg	Manganese (Mn), mg/kg	Selenium (Se), mg/kg	Sodium (Na), mg/kg	Zinc (Zn), mg/kg
1			ГОСТ 30178-96					ГОСТ 30178-96
2	ДСТУ 7670:2014, ДСТУ ISO 11885:2005		ДСТУ 7670:2014, ДСТУ ISO 11885:2005				ДСТУ 7670:2014, ДСТУ ISO 11885:2004	
3	DIN EN 15621:2017					DIN EN 14627:2005	DIN EN 15621:2017	
4	МВВ. 7.2-16-В						МВВ. 7.2-16-В	
5	МВ-ВЛ/ТЕ-5.8-01						МВ-ВЛ/ТЕ-5.8-01	
6	МІ.С3.7.2.01-019							
7	МВВ № 01-15						МВВ № 01-15	
8	МВ.БЛС 7.2-04.09.01							
9	АГМ-17		АГМ-17					АГМ-17
10	DIN EN 15621:2017						DIN EN 15621:2017	

9.2. An instrumental method of analysis

Laboratory number	Calcium (Ca), mg/kg	Cobalt (Co), mg/kg	Cuprum (Cu), mg/kg	Iron (Fe), mg/kg	Manganese (Mn), mg/kg	Selenium (Se), mg/kg	Sodium (Na), mg/kg	Zinc (Zn), mg/kg
1			Полумнева атомно-абсорбційна спектометрія					Полумнева атомно-абсорбційна спектометрія
2	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)		Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)				Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)	
3	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)					Атомна емісія з генеруванням гідридів	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)	
4	(ICP-OAES)						(ICP-OAES)	
5	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)						Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)	
6	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)							
7	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)						Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)	
8	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)							
9	ICP-OES		ICP-OES					ICP-OES
10	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)						Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)	

9.3. Method of sample decomposition

Laboratory number	Method of sample decomposition
1	Мікрохвильовий (microwave)
2	Розкладання мікрохвильовою системою MARS 6
3	Мікрохвильова кислотна мінералізація під тиском
4	Мокра мінералізація
5	DIN EN 13805-2014 мінералізація при підвищеному тиску
6	Система мікрохвильової підготовки MARS
7	Кислотна мінералізація
8	Мікрохвильове розкладання в азотній кислоті під тиском
9	Мікрохвильове розкладання
10	Мікрохвильовий метод мінералізації

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