METROLOGY SERVICE

Director
Metrology service Ltd.

Bozhko Nataliia
November 21th 2019

PROFICIENCY TESTING PT.UA.2.10.2019

ANIMAL FEEDING STUFFS (MICROELEMENTS)

PROFICIENCY TESTING REPORT

ROUND 1 NOVEMBER 2019

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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.

2.3. This is the final report on the PT.UA.2.10.2019 Round 1 held in october-november 2019. This report is issued according to ISO/IEC 17043[1] and PT.UA.2.10.2019 Round 1 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 11 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 1. 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 11.11.2019 according to schedule of proficiency testing programme PT.UA.2.10.2019 Round 1.

3.3.2. Each produced and identified sample was hermetically sealed.

3.3.3. A total of 11 participants in 2 countries received one sample. Results were returned from 11 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 11,76% (6 results) of all results in this round are considered to be unsatisfactory.

3.5.6. Participant №12 stated the result for «Lead (Pb), mg/kg» and «Cadmium (Cd), mg/kg» like «<0,001» and «<0,0001» in accordance. These results were assessed by the Provider as quantitative.

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. Zinc (Zn), mg/kg

Zinc (Zn), mg/kg										
Дослідження гомогенності/Homogenity test										
Аналіз викидів за тестом Кохрана(C -тест)/Cohran's C test for outliers						Аналіз на 'достатню однорідність'/Test for 'sufficient homogenity'				
Sample number	Результат/ Result A	Результат/ Result B	Average	SD²		Номер зразку /Sample number	Результат/ Result A	Результат/ Result B	SUM	Difference²
1	2079	2188	2133,50	5940,5000	0,00	1	2079,00	2188,00	4267,00	11881,0000
2	2121	2181	2151,00	1800,0000	0,00	2	2121,00	2181,00	4302,00	3600,0000
3	2182	2154	2168,00	392,0000	0,00	3	2182,00	2154,00	4336,00	784,0000
4	2302	2400	2351,00	4802,0000	0,00	4	2302,00	2400,00	4702,00	9604,0000
5	2164	2102	2133,00	1922,0000	0,00	5	2164,00	2102,00	4266,00	3844,0000
6	2186	2248	2217,00	1922,0000	0,00	6	2186,00	2248,00	4434,00	3844,0000
7	2324	2296	2310,00	392,0000	0,00	7	2324,00	2296,00	4620,00	784,0000
										34341,0000
Mean	2209,071		Worst pair	5940,5000		Mean	2209,071			
Max	2400,00		SUM of SD²	17170,5000		Max	2400,00			
Min	2079,00		C	0,3460		Min	2079,00			
			Ccr, 5%	0,7271						
			Ccr, 1%	0,8376		Analytical variance S²a	2452,9286	SD	92,4333	
			Conclusion			Sanal	49,5270	RSDR	4,1843	
			5%	PASS		Ssums	31300,1429			
			1%	PASS		MSb	15650,0714			
					Between sample variance S²sam		6598,5714			
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	4,7001
	120ppb<C<13.8%, HORWITZ	27,7291
	C<120 ppb	485,995714
MASS NEGATIVE POWER FOR HORWITZ EQUATION(%=2, ppb=9,ppm=6)		2
	SD	89,0710
1	Trial SD	278,5880
	Target SD chosen	278,5880
	σ²all	6985,014637
	Replicates	7
	F1	2,1
	F2	1,43
	Critical value	18176,2186
	Between sample variance S²sam	6598,5714
	Sufficient homogenity test	PASS

4.6. Data for all analytes

	Zinc (Zn), mg/kg	Iron (Fe), mg/kg	Lead (Pb), mg/kg	Cadmium (Cd), mg/kg	Copper (Cu), mg/kg
Homogenity and stability (Гомогенність та стабільність)					
Cohran's 'C' test (С-тест "Кохрана")					
Crtitical value (5%,7pairs)=0,7271	0,3460	0,6857	0,30596	0,263053	0,4867
Mean Result	2209,0714	216,9264	0,39919	0,046350	164,5679
Conclusion (Висновок)	PASS	PASS	PASS	PASS	PASS
Analytical variance test (тест аналітичної дисперсії)					
S^2anal	2452,9286	72,7093	0,00014	0,000001	44,9452
Sanal	49,5270	8,5270	0,01184	0,001199	6,7041
S^2sample	6598,571	350,1363	0,00003	0,000004	104,7402
σ_p	278,5880	54,0790	0,07300	0,013000	19,7320
σ_p source	Trial SD	Trial SD	Trial SD	Trial SD	Trial SD
σ^2all	6985,0146	263,2084	0,00048	0,000015	35,0417
Critical value	18176,2186	656,7120	0,00121	0,000034	137,8591
Conclusion (Висновок)	PASS	PASS	PASS	PASS	PASS

5. DATA SUMMARY

	Zinc (Zn), mg/kg	Iron (Fe), mg/kg	Lead (Pb), mg/kg	Cadmium (Cd), mg/kg	Copper (Cu), mg/kg
No of Results	11	10	10	9	11
No of Results |z|>3	2	0	2	1	1
No of Results |z|>3, %	18,182	0,000	20,000	11,111	9,091
Mean	2014,128	215,589	0,517	0,051	181,650
Min	81,000	86,500	0,001	0,000	11,000
Max	2936,900	301,000	2,190	0,290	243,600
SD	785,240	67,255	0,738	0,091	60,223
Median	2085,010	231,000	0,187	0,020	192,600
Robust mean (assigned value)	2250,826	222,734	0,188	0,024	197,319
Robust SD	278,588	54,079	0,073	0,013	15,400
SD from method (Tr.SD)	N/A	N/A	N/A	N/A	N/A
SD from Horwitz eq.	112,679	15,793	0,039	0,005	14,249
Target SD	278,588	54,079	0,073	0,013	19,732
Source of target SD of PT	Trial SD	Trial SD	Trial SD	Trial SD	Trial SD

6. RAW DATA

Laboratory number	Zinc (Zn), mg/kg	Iron (Fe), mg/kg	Lead (Pb), mg/kg	Cadmium (Cd), mg/kg	Copper (Cu), mg/kg
1	1985,00		1,560	0,007	212,50
2	2350,00	260,00			178,00
3	1130,90	282,97	0,149	0,029	213,93
4	2530,27	204,45	0,268	0,016	204,30
6	2398,00	226,00	0,399	0,046	165,00
7	2523,33	190,26	2,190	0,290	192,04
8	2070,00	236,00	0,182		187,90
9	2065,00	243,50	0,191	0,020	192,60
10	2085,01	125,21	0,089	0,036	197,28
11	81,0	86,5	0,14	0,014	11,0
12	2936,90	301,00	<0,001	<0,0001	243,60

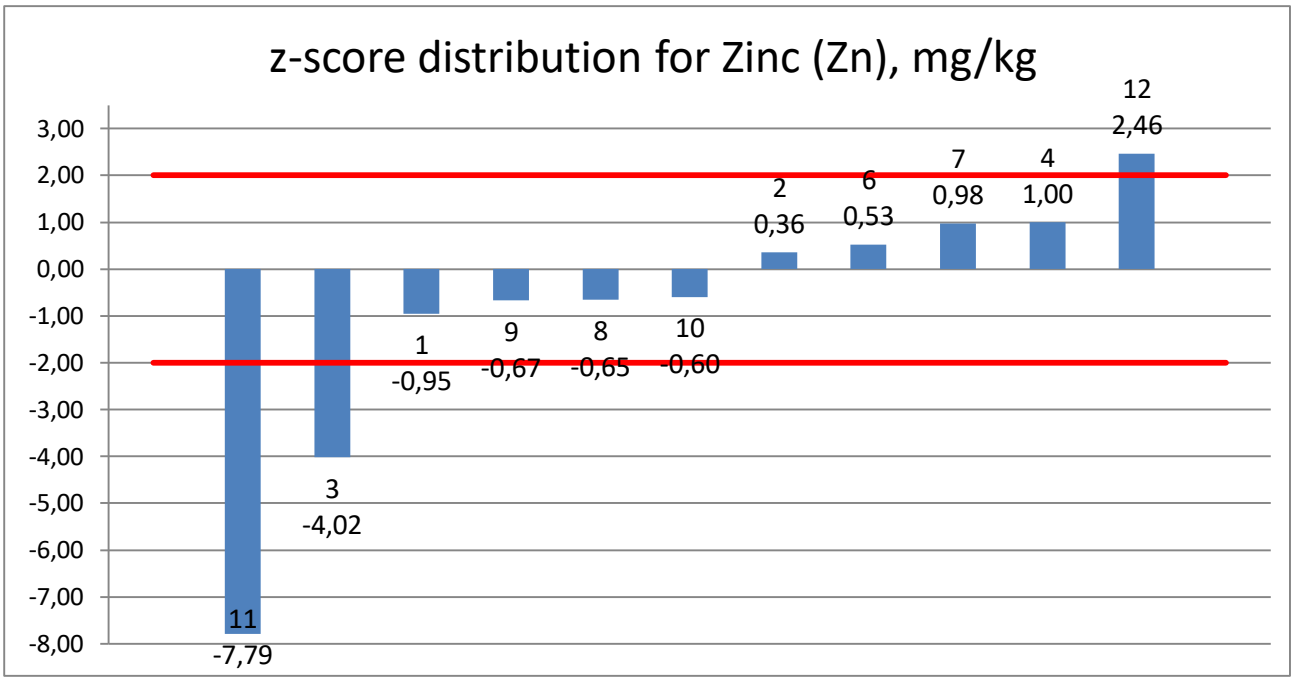
7. Z SCORES

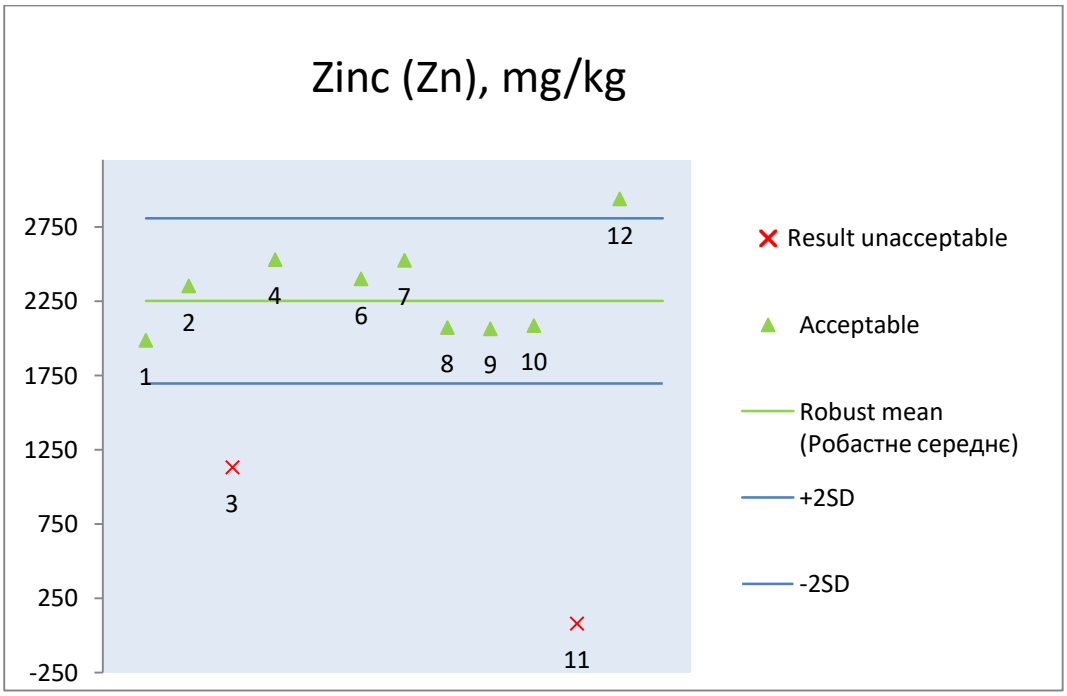
Laboratory number	Zinc (Zn), mg/kg	Iron (Fe), mg/kg	Lead (Pb), mg/kg	Cadmium (Cd), mg/kg	Copper (Cu), mg/kg
1	-0,95		18,72	-1,26	0,77
2	0,36	0,69			-0,98
3	-4,02	1,11	-0,53	0,45	0,84
4	1,00	-0,34	1,09	-0,63	0,35
6	0,53	0,06	2,88	1,74	-1,64
7	0,98	-0,60	27,32	20,69	-0,27
8	-0,65	0,25	-0,08		-0,48
9	-0,67	0,38	0,04	-0,28	-0,24
10	-0,60	-1,80	-1,35	0,96	0,00
11	-7,79	-2,52	-0,66	-0,75	-9,44
12	2,46	1,45	-2,55	-1,82	2,35

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.

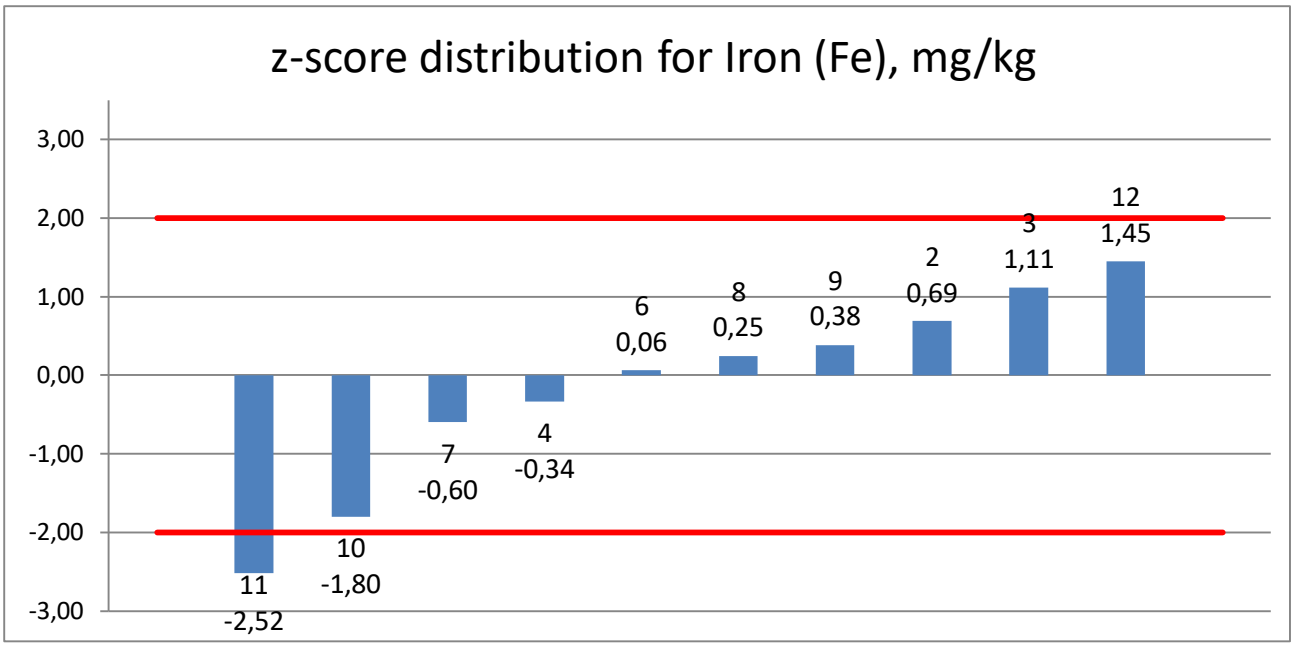
8. Z SCORE PLOTS AND RESULTS CHARTS.

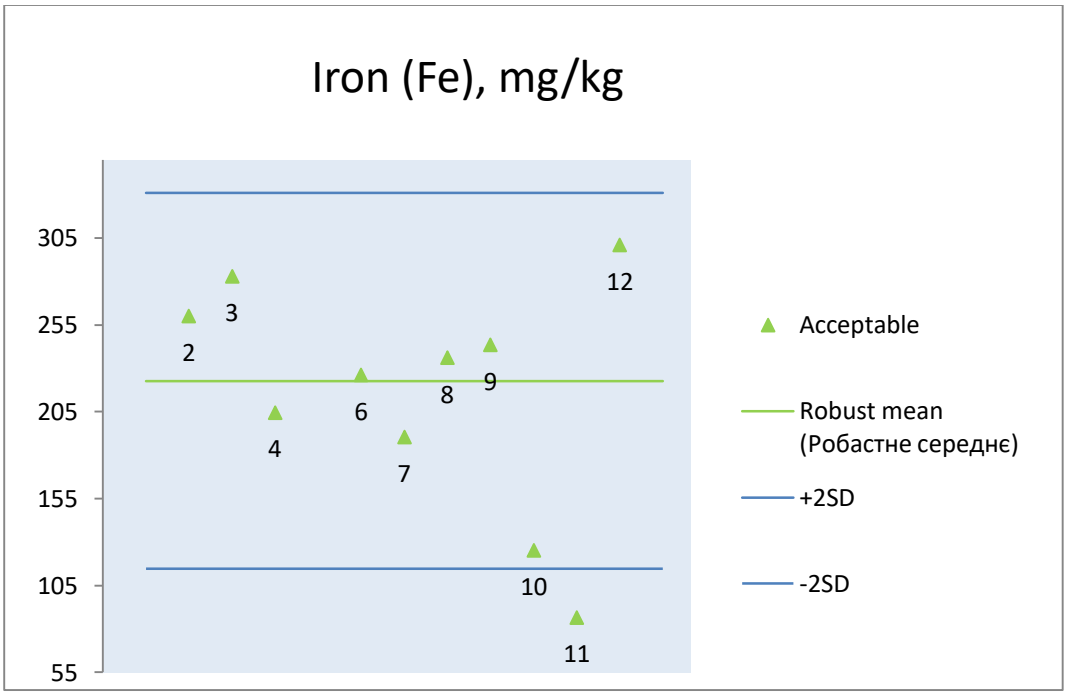
8.1. Zinc (Zn), mg/kg



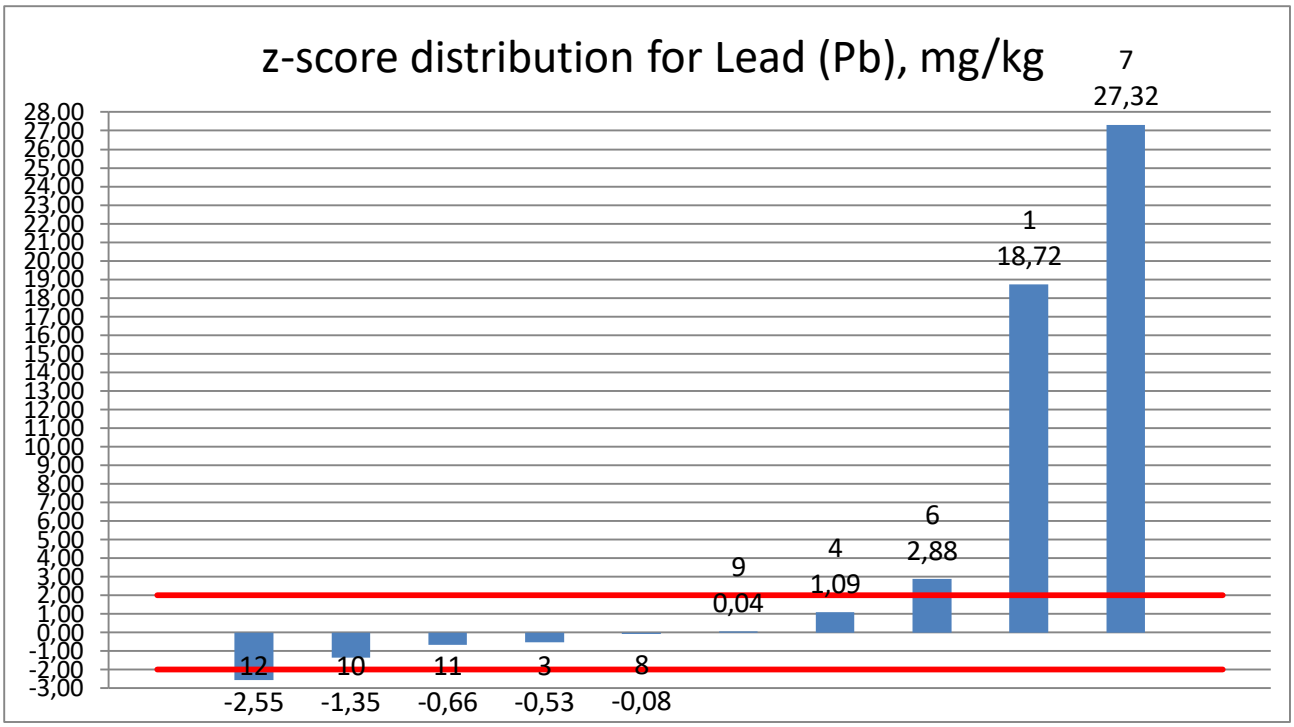


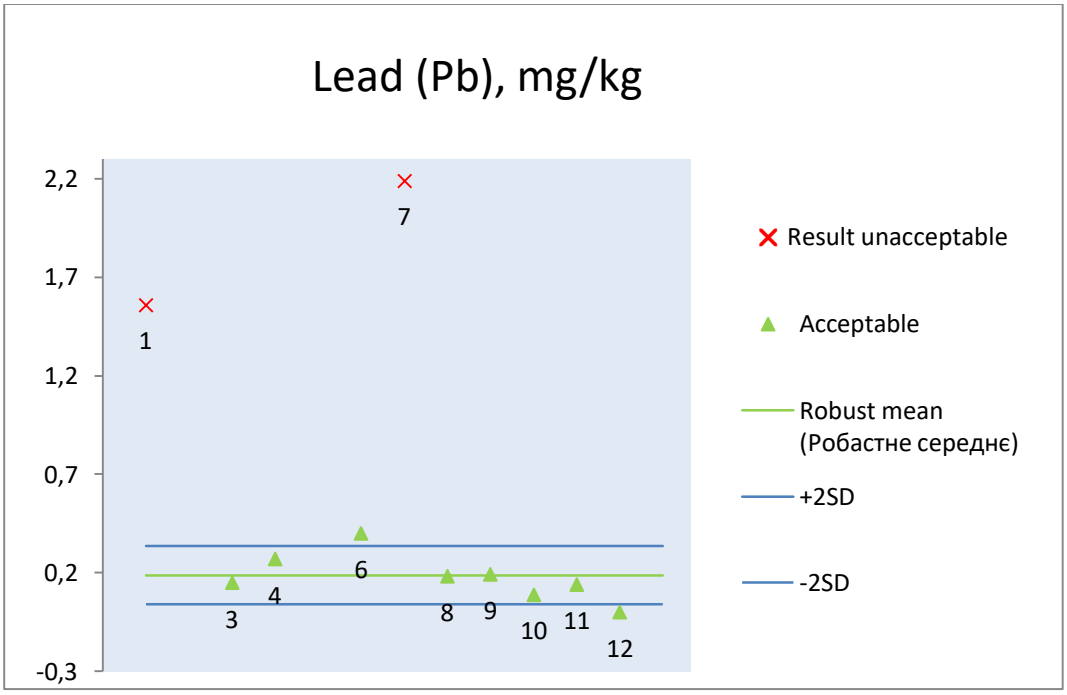
8.2. Iron (Fe), mg/kg



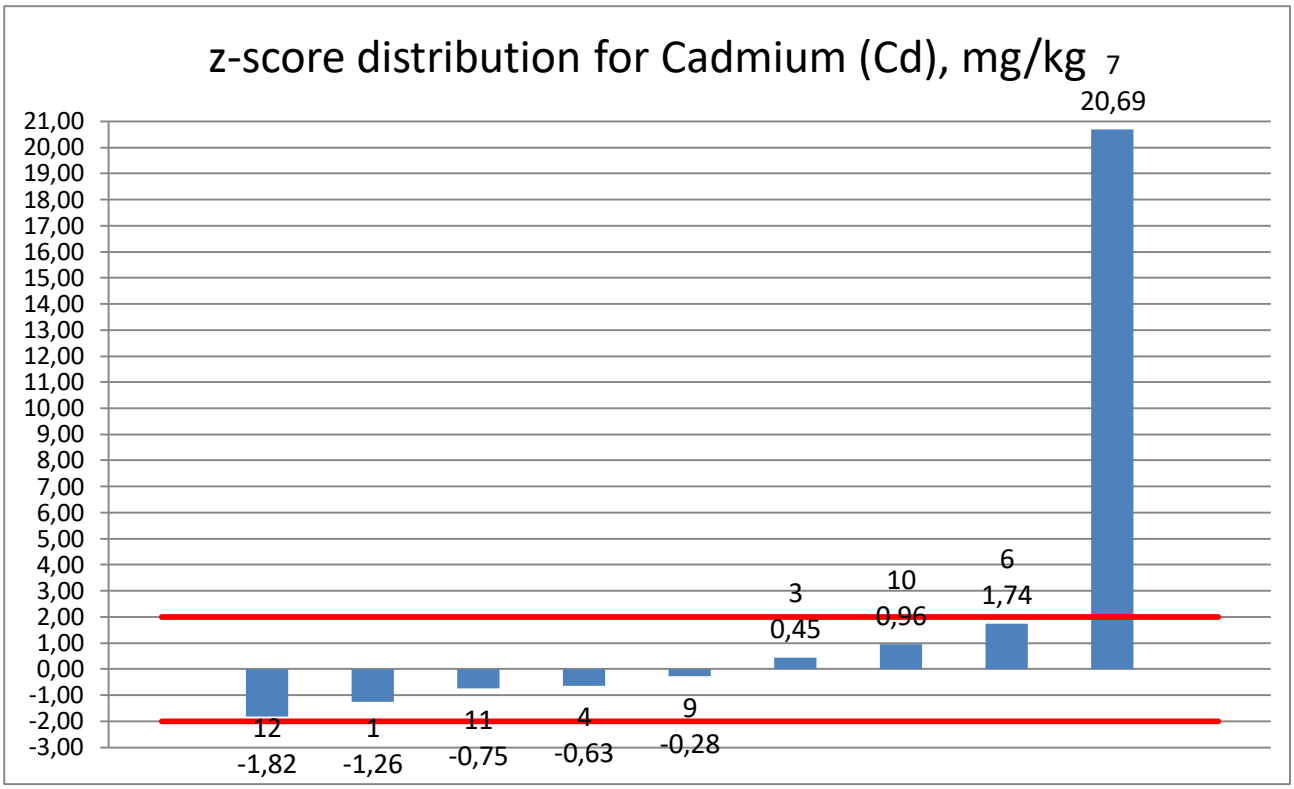


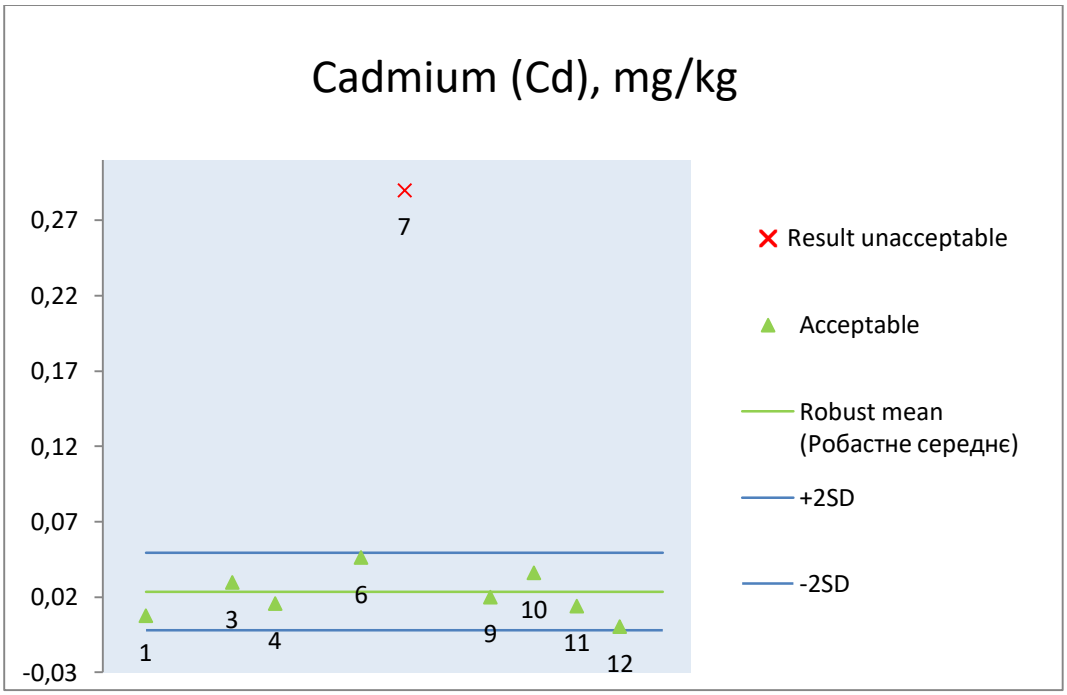
8.3. Lead (Pb), mg/kg



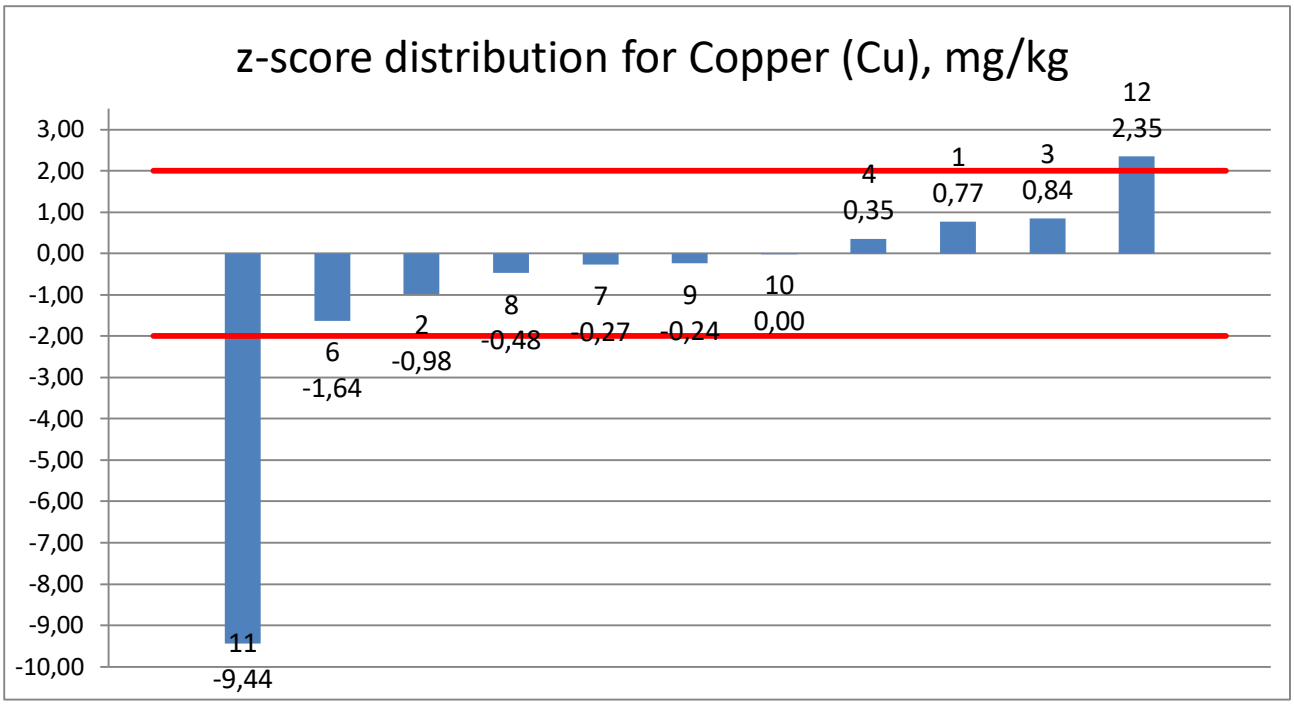


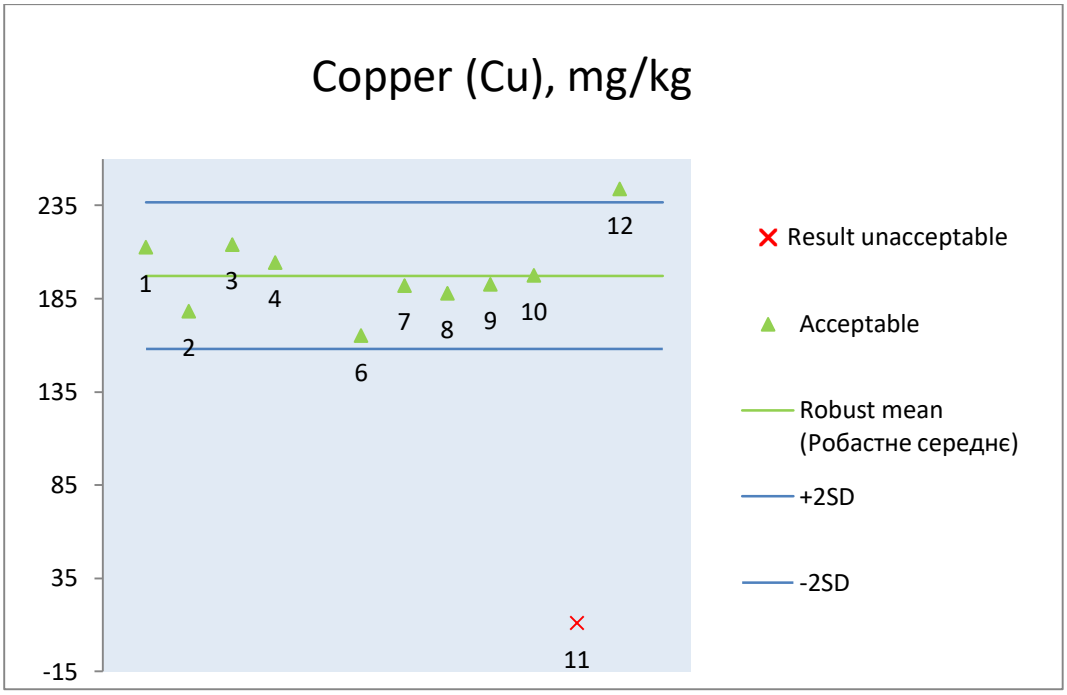
8.4. Cadmium (Cd), mg/kg





8.5. Copper (Cu), mg/kg





9. REFERENCE INFORMATION

9.1. Methods

Laboratory number	Zinc (Zn), mg/kg	Iron (Fe), mg/kg	Lead (Pb), mg/kg	Cadmium (Cd), mg/kg	Copper (Cu), mg/kg
1	МВВ 081-12/04-98		МВВ 081-12/04-98		
2	ДСТУ 8123:2015/ИСО 6869:200				ДСТУ 8123:2015/ ИСО 6869:200
3	ГОСТ 30178-96		ПВ ВЛ -5.4/06		ГОСТ 30178-96
4	EN 14084:2003		EN 15550:2017		EN 14084:2003
6	ПВ.БЛС 7.2-04/09				
7	ДСТУ 8123:2015		ГОСТ 30178-96/ДСТУ 7670:2014		ДСТУ 8123:2015
8	DIN EN 15621:2017		DIN EN 14083:2003		DIN EN 15621:2017
9	ПВ. ЧРДЛ ДПСС 7.2-92				
10	МВВ № 01-15				
11	GOST 33824-2016	GOST 30178-96	GOST 33824-2016		
12	МВ-ВЛ/ТЕ-5.8-01/ДСТУ ISO 11885:2005				

9.2. An instrumental method of analysis

Laboratory number	Zinc (Zn), mg/kg	Iron (Fe), mg/kg	Lead (Pb), mg/kg	Cadmium (Cd), mg/kg	Copper (Cu), mg/kg
1	Метод інверсійної вольтамперометрії		Метод інверсійної вольтамперометрії		
2	Полуменева атомно-абсорбційна спектрометрія Flame - AAS				Полуменева атомно-абсорбційна спектрометрія Flame - AAS
3	Полуменева атомно-абсорбційна спектрометрія Flame - AAS		Атомно-абсорбційна спектрометрія з електротермічною атомізацією (AAS-ETA)		Полуменева атомно-абсорбційна спектрометрія Flame - AAS
4	Полуменева атомно-абсорбційна спектрометрія Flame - AAS		Атомно-абсорбційна спектрометрія з електротермічною атомізацією (AAS-ETA)		Полуменева атомно-абсорбційна спектрометрія Flame - AAS
6	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)				
7	Полуменева атомно-абсорбційна спектрометрія Flame - AAS				
8	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)		Атомно-абсорбційна спектрометрія з електротермічною атомізацією (AAS-ETA)		Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)
9	АЕС-ІЗП				
10	Атомно-емісійна спектрометрія з індуктивно зв'язаною плазмою (ICP-OAES)				
11	Voltamperometria	AAC	Voltamperometria		
12	Оптико-емесійний спектрометр з індуктивно зв'язаною плазмою (ICP-OES) (PerkenElmer Avio 500)				

9.3. Method of sample decomposition

Laboratory number	Method of sample decomposition
1	ДСТУ 7670:2014 Сировина і продукти харчові. Готування проб. Мінералізація для визначення вмісті токсичних елементів.
2	Сухе озолення в муфелі при 550 С. 4-5 годин. Потім оброблення соляною кислотою.
3	Мікрохвильовий метод мінералізації
4	Мокрое озоление
6	Розкладання у мікрохвильовій печі під тиском
7	Суха мінералізація
8	Мікрохвильове перетравлення згідно DIN EN 13805:2014
9	Метод мікрохвильової мінералізаціїі
10	Кислотна мінералізація
11	Wet ashing
12	DIN EN 13805-2014 (Система мікрохвильового розкладання зразків MARS-6)

10. NORMATIVE REFERENCE

1. ISO/IEC 17043:2010 Conformity assessment – General requirements for proficiency testing.
2. Analytical Methods Committee, Robust Statistics – How not to reject outliers Part 1. Basic Concepts, Analyst, 1989, 114, 1693-1697.
3. FOOD ANALYSIS PERFORMANCE ASSESSMENT SCHEME (FAPAS). Protocol for the organization and analysis of data, sixth edition, 2002.
4. Fearn, T. and Thompson, M, A new test for 'sufficient homogeneity', Analyst, 2001, 126, 1414-1417.
5. ISO 13528:2015 Statistical methods for use in proficiency testing by interlaboratory comparisons.
6. ISO Guide 35:2017 Reference materials – Guidance for characterization and assessment of homogeneity and stability.
7. ILAC Discussion Paper on Homogeneity and Stability Testing, April 2008.