INSTITUTE OF PUBLIC HEALTH
SKOPJE, REPUBLIC OF MACEDONIA (FYROM)

PROFICIENCY TESTING SCHEME: DRINKING WATER
FINAL REPORT

Report No: IPA 2011 PT 2

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REPUBLIC OF MACEDONIA, FYROM

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1. INTRODUCTION

Drinking water or potable water is water safe enough to be consumed by humans or used with low risk of immediate or long term harm. There are a variety of trace elements present all potable water, some of which play a role in metabolism. For example sodium, potassium and chloride are common chemicals found in small quantities in most waters, and these elements play a role in body metabolism. Other elements such as fluoride, while beneficial in low concentrations, can cause dental problems and other issues when present at high levels. Others such as lead, cadmium, mercury, arsenic, antimony, aluminum are considered toxic for humans. Therefore Maximum Allowed Values are set for trace elements, anions and other chemical and biological substances for drinking water.

Proficiency testing (PT) aims to provide an independent assessment of the competence of participating laboratories. Together with the use of validation methods proficiency testing is an essential element of laboratory quality assurance. Proficiency testing is defined in ISO/IEC 17043:2010 as the use of inter-laboratory comparisons to determine the performance of individual laboratories for specific tests of measurements and to monitor laboratories continuing performance. As described in ISO/IEC 17025, a laboratory participation in proficiency testing activities is requirement of the standard. Participation in proficiency testing activities also provides a valuable feedback in internal monitoring of a laboratory's quality system. Through these activities laboratory can verify its competence to perform specific test.

Within the "IPA 2011 – Regional Quality Infrastructure in Western Balkans and Turkey" project, Proficiency Testing Scheme for Drinking Water was organized by INSTITUTE OF PUBLIC HEALTH Chemistry Group Laboratory under the auspices of University of Ljubljana, Faculty of Electrical Engineering - Laboratory of Metrology and Quality.
Under this study Proficiency Test PT 2 was operated in accordance with ISO/IEC 17043. Participants in PT 2 were asked to measure the amount content of elements: Al, As, Cd, Cr total, Cu, Fe, Mn, Ni, Pb, Zn and Hg, and anions: fluoride, chloride, nitrite, nitrate, phosphate and sulphate in drinking water.

2. ORGANIZATION and DESIGN

Scheme Coordinator

Day - to - day operation of the scheme is the responsibility of Scheme Coordinator.

Coordinator: Vesna Kostik.

Technical Group

Technical group consists of members who are experienced in the field of chemical analysis of metals and anions.

Technical Group: Vesna Kostik, Biljana Manevska and Irena Bojadzieva.

Scheme Coordinator and technical group are responsible for preparation of test material, reporting and technical functions.

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3. PARTICIPANTS

PT 2 was opened to laboratories from Montenegro and Republic of Macedonia supported by IPA 2011 project. Eighteen laboratories participated in PT 2: Six laboratories were from Montenegro and twelve laboratories were from Republic of Macedonia.

4. INSTRUCTIONS TO THE PARTICIPANTS

A technical protocol was send to all participants in PT 2, at the same date of the sample distribution providing information concerning the sample, sample storage, the recommended measurement method and confidentiality. Additionally a report form was distributed for reporting the result and additional information requested from the participants. At the same time, the same test material of drinking water was send to independent accredited laboratories for trace metals and anion analysis.

Appendix A shows the technical protocol and report form for PT 2.

5. SAMPLES

Natural spring water was used in this PT scheme. The approximate composition of the natural spring water used for the preparation of the samples is given in the technical protocol (see Appendix A).

6. METHODS AND INSTRUMENTATION USED

Participants were free to use method of their choice. It was recommended to use the same method and operators with routine analysis. Participants were asked to treat the PT material in the same way as the routine sample, and to state their method (instrumentation) when reporting the results.

Methods (instrumentation) used in the analysis by the participants are given in Table 1 - Table 2.

Table 1. Methods/Instruments used in trace metals analysis by the participants

Lab. code	Pb	Cd	Cu	Fe	Mn	Zn	Ni	Cr total	Al	As	Hg
1	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	-	-
2	GF ASS	GF ASS	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	GF ASS	Mercury analyzer
3	-	-	-	Spectrophotometry	-	-	-	-	-	-	-
4	-	-	-	100796 Iron Test Method	101739 Manganese Test Method	-	-	-	-	-	-
5	-	-	-	Standard Method P-V-17/C	-	-	-	-	-	-	-
6	GFAAS	GFAAS	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	-	DMA
7	ICP	ICP	ICP	Merck test 1.14761	ICP	ICP	ICP	ICP	ICP	-	-
8	EN 14028:2003	EN 14028:2003	EN 14028:2003	HACH DR 4000 Method 8008	HACH DR 4000 Method 8149	HACH DR 4000 Method 8009	HACH DR 4000 Method 8150	-	HACH DR 4000 Method 8326	-	-
9	MKC EN ISO 15586: 2009 (AAS-GF)	MKC EN ISO 15586: 2009 (AAS-GF)	-	MKC EN ISO 15586: 2009 (AAS-GF)	MKC EN ISO 15586: 2009 (AAS-GF)	-	MKC EN ISO 15586: 2009 (AAS-GF)	-	MKC EN ISO 15586: 2009 (AAS-GF)	MKC EN ISO 15586: 2009 (AAS-GF)	-
10	-	-	-	Spectrophotometric Merck test 1.14761.001	Spectrophotometric Merck test 1.14770.001	-	-	-	-	-	-

Table 1. Methods/Instruments used in trace metals analysis by the participants (continued)

Lab. code	Pb	Cd	Cu	Fe	Mn	Zn	Ni	Cr total	Al	As	Hg
11	-	-	-	Photometric SQ 118	Photometric SQ 118	-	-	Photometric SQ 118	Photometric SQ 118	-	-
12	-	-	-	Spektroquant test 1.14761	Spektroquant test 1.14770	-	-	-	-	-	-
13				HACH- 8008	HACH- 8149						
14	MKC EN ISO 11885: 2007	MKC EN ISO 11885: 2007	MKC EN ISO 11885: 2007	HACH- 8008	MKC EN ISO 11885: 2007	MKC EN ISO 11885: 2007	MKC EN ISO 11885: 2007	MKC EN ISO 11885: 2007	MKC EN ISO 11885: 2007	MKC EN ISO 11885: 2007	-
15	MS-ICP	MS-ICP	MS-ICP	MS-ICP	MS-ICP	MS-ICP	MS-ICP	MS-ICP	MS-ICP	MS-ICP	-
16	ICP- AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	CV-AAS
17	ETAAS	ETAAS	FAAS	FAAS	FAAS	FAAS	ETAAS	ETAAS	-	ETAAS	CV-AAS
18	ASTM D 3559 – 03 / D	ASTM D 3557 – 02 / C	ASTM D 1688 – 02 / C	ASTM D 1068 – 03 / C	ASTM D 858 – 02 / C	ASTM D 1691 – 02 / A	ASTM D 1886 – 03 / C	ASTM D 1687 – 02 / C	-	ASTM D 2972 – 03 / C	-

Table 2. Methods/Instruments used in the anion analysis by the participants

Laboratory Code	F^-	PO_4^{-3}	Cl^-	NO_3^-	NO_2^-	SO_4^{-2}
1	Ion Chromatography	Spectrophotometry	Ion Chromatography	Spectrophotometry	Spectrophotometry	Ion Chromatography
2	Ion selective electrode	UV-VIS	Volumetry	UV-VIS	UV-VIS	UV-VIS
3	-	Spectrophotometry	Titration with Hg(NO3)2	Spectrophotometry	Spectrophotometry	Spectrophotometry
4	Fluoride Test Method 114598	Phospahe Test (o-phosphat) Test Method 114848	Chloride Test Method 1114897	Standard Methods for the Examination of Water and Wastewater, 19th Edition 1995	Nitrite Test Method 114776	-
5	-	-	Standard Method P-V-19/B	Standard Method P-V-31/C	-	-
6	Ion Chromatography	Ion Chromatography	Ion Chromatography	Ion Chromatography	Ion Chromatography	Ion Chromatography
7	Merck Test 1.14557	Merck Test 1.14848	ISO 9297:1989	APHAA4500-NO3B	Merck Test 1.14776	Merck Test 1.14548
8	Spectrophotometry HACH DR 4000 Method 8029	-	ISO 9297:1989 Volumetry – Titration with AgNO3	Spectrophotometry HACH DR 4000 Method 8039	Spectrophotometry HACH DR 4000 Method 8507	Spectrophotometry HACH DR 4000 Method 8051
9	-	-	ISO 9297	Spectrophotometry	Spectroquant nitrite test 1.14776.0002	-
10	-	-	ISO 9297	Spectrophotometric Merck Test 1.14773.0001	Spectrophotometric Merck Test 1.14776.0002	-
11	-	-	Photometry SQ 118	Photometry SQ 118	Photometry SQ 118	Photometry SQ 118
12	-	-	Spectroquant chloride test 1.14897	Spectroquant nitrate test 1.14773	Spectroquant nitrite test 1.14776	-
13	-	-	HACH-8113	HACH-8171	HACH-8507	HACH-8051
14	HACH- 8029	HACH- 8048	ISO 9297:1984	HACH- 8039	HACH- 8507	HACH- 8051
15	-	MS-ICP	EPA 325.3	Spectrophotometry	EPA 354.1	EPA 375.4
17	-	-	Volumetry	Spectrophotometry	Spectrophotometry	Spectrophotometry
18	US EPA 340.1	ISO 8466-1	MKS EN ISO 9297:2007	APHA 4500-B	US EPA 354.1	US EPA 375.4

7. CONFIDENTIALITY

In order to ensure confidentiality, each participant in the scheme was allocated with a unique laboratory code. All information submitted by the participants to the proficiency testing provider, were treated as confidential.

8. RESULTS and EVALUATION of PERFORMANCE

The results submitted by the participants were statistically analysed in order to provide an assigned value for each analyte. The assigned values were than used in combination with the standard deviation for proficiency assessment (σ), to calculate a z- score for each result. The procedure follows that recommended in the IUPAC International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.

The International Standard recommends the use of robust statistical methods when it is considered that they are the most appropriate methods to calculate assigned (reference) values. In this study the assigned values were determined from median of PT 2 participants' results and from accredited laboratories results (see Appendix C).

The standard deviation for proficiency assessment was set with reference to performance requirements in Water Regulations, at a value that reflects best practice for the analysis in question.

For this exercise standard deviation for proficiency testing assessment for trace metals were determined as different percentage of reference values depending on the parameters. Standard deviation values for Cu, Mn and Pb was determined as 7.5 % of reference values; for Al, As, Cd, Cr, Ni and Zn was determined as 10 % of reference values; for Fe was determined as 12 % and for Hg was determined as 15 % of reference values respectively.

Standard deviation for proficiency testing assessment for anions was derived from the Horwitz Equation:

$$\sigma = 0.02c^{0.8495}$$

Where *c* is the assigned value of the analyte expressed as a dimensionless mass ratio (e.g. 1 µg/g = 1 ppm = 10^{-6}).

Participant's z-scores were calculated using the following equation:

$$z = \frac{x - X}{\sigma}$$

Where; x= participant's result

X = Assigned value

σ = standard deviation for proficiency testing assessment

For z-score the following interpretation is given to results.

$\|z\| \leq 2.00$	Satisfactory result
$2.00 < \|z\| < 3.00$	Questionable result
$\|z\| \geq 3.00$	Unsatisfactory result

Participant's results are given in Table 3 – Table 5. Graphical representations of the data are provided in Figure 1 – Figure 17.

Distribution of the z-scores and the results for trace metals and anion analysis in drinking water are given in Table 6 - Table 9, respectively.

Table 3 Participant's results and z- scores for trace metals in drinking water

Laboratory Code	**Pb**			**Cd**			**Cu**			**As**			**Cr**			**Fe**		
	Reference Value = 27.05 µg/l			**Reference Value= = 7.13 µg/l**			**Reference Value = 30.3 µg/l**			**Referenced Value= = 29.3 µg/l**			**Reference Value = = 30.17 µg/l**			**Reference Value= = 180.3 µg/l**		
	σ = 2.03 µg/l			**σ = 0.7 µg/l**			**σ = 2.27 µg/l**			**σ = 2.93 µg/l**			**σ = 3.02 µg/l**			**σ = 21.6 µg/l**		
	X	**S**	**Z**	**X**	**S**	**Z**	**X**	**S**	**Z**	**X**	**S**	**Z**	**X**	**S**	**Z**	**X**	**S**	**Z**
1	24.48	2.08	-1.27	7.12	0.402	-0.01	28.69	0.493	-0.71	-	-	-	25.22	1.048	-1.64	163.7	3.203	-0.77
2	26.32	0.1075	-0.73	7.328	0.0583	0.28	31.31	0.0777	0.44	30.50	0.175	0.41	29.64	0.0252	-0.17	183.73	0.5774	0.16
3	-	-	-	-	-	**-**	-	-	-	-	-	-	-	-	-	165	7.7/4.7%	-0.7
4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	190	10	0.44
5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	129.8	0.0000	**-2.34**
6	25.8	0.9	-0.62	7.1	0.35	-0.04	26.77	0.46	-1.55	-	-	-	29.99	1.15	-0.06	156.2	0.75	-1.11
7	31	-	1.94	7	-	-0.18	36	-	**2.51**	-	-	-	26	-/	-1.28	194	3	0.63
8	14.46167	0.517201	**-6.2**	8.265	0.19953	1.62	21.623	0.129099	**-3.8**	-	-	-	-	-	**-**	31	0.894427	**-6.91**
9	29.15	1.041	1.03	6.90	0.015	-0.32	-	-	-	31.03	1.003	0.59	-	-	-	152.5	0.516	-1.28
10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	200	16	0.91
11	-	-	-	-	-	-	-	-	-	-	-	-	n.d.	-	-	190	0.004	0.45
12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	170	±18	-0.47
13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	180	20	-0.01
14	36.13	3.0	**4.47**	6.7	0.99	- 0.61	36.2	1.27	**2.59**	15.25	0.1	**-4.79**	31.3	2.0	0.37	180	2.8	-0.01
15	24.4	0.735	-1.3	4.2	0.098	**-4.18**	16.4	1.42	**-6.12**	19.4	0.164	**-3.38**	21.9	0.393	**-2.74**	165	14.3	-0.7
16	25.57	1.74	-0.72	5.15	0.29	**-2.83**	30.92	0.16	0.27	20.17	0.94	**-3.12**	22.66	0.47	**-2.49**	125.5	1.53	**-2.53**
17	36.55	2.547	**4.68**	7.126	0.290	0	36	0.100	**2.51**	32.23	2.136	1.0	26.73	1.183	-1.14	177.0	2.00	-0.15
18	20.59	0.15	**-3.18**	5.30	0.26	**-2.6**	33.02	1.48	1.19	35.66	0.685	**2.17**	30.5	2.7	0.11	138	2.84	-1.96

Table 4. Participant's results and z- scores for trace metals in drinking water

Laboratory Code	Al			Mn			Zn			Hg			Ni		
	Reference Value = 154 µg/l			Reference Value = 30.4 µg/l			Referenced Value = 359.6 µg/l			Reference Value = 3.43 µg/l			Reference Value = 30.8 µg/l		
	σ = 15.4 µg/l			σ = 2.28 µg/l			σ = 35.9 µg/l			σ = 0.51 µg/l			σ = 3.08 µg/l		
	X	**S**	**Z**	**X**	**S**	**Z**	**X**	**S**	**Z**	**X**	**S**	**Z**	**X**	**S**	**Z**
1	122.9	4.831	**-2.02**	29.76	0.904	-0.28	355.0	11.05	-0.13	-	-	-	27.68	1.42	-1.01
2	153.00	0.0529	-0.06	31.02	0.0721	0.27	396.30	0.2517	1.02	3.35	0.010	-0.16	32.50	0.2646	0.55
3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	29.9	3.1	-0.22	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	178.8	0.98	1.61	28.8	0.2	-0.70	358.3	1.5	-0.04	2.898	0.14	-1.04	28.10	0.43	-0.88
7	188	-	**2.21**	29	-	-0.61	343	-	-0.46	-	-	-	27	-	-1.23
8	36.333	2.2509	**-7.6**	20	0.894427	**-4.56**	101.1	1.1690	**-7.2**	-	-	-	44.8333	0.983192	**4.55**
9	108.48	1.258	**-2.9**	28.93	0.291	-0.64	-	-	-	-	-	-	20.93	0.965	**-3.2**
10	-	-	/	33	/	1.14	-	-	-	-	-	-	-	-	-
11	200	0.008	**2.99**	40	0.005	**4.21**	-	-	-	-	-	-	-	-	-
12	-	-	-	≤ 10	± 37	-	-	-	-	-	-	-	-	-	-
13	-	-	-	29	3.3	-0.61	-	-	-	-	-	-	-	-	-
14	183.0	16.3	1.88	31.9	5.8	0.65	340.0	10.2	-0.54	-	-	-	30.6	3.18	-0.06
15	111.8	0.894	**-2.7**	20.9	0.261	**-4.16**	252	0.079	**-2.99**	-	-	-	19.3	0.702	**-3.73**
16	120.0	0.66	**-2.2**	24.54	0.07	**-2.57**	239.7	1.05	**-3.34**	4.42	0.04	1.94	24.12	0.58	**-2.17**
17	-	-	-	34	1.00	1.58	352.0	0.10	-0.21	3.129	0.02	-0.59	24.62	2.240	-2.00
18	-	-	-	33.59	2.73	1.39	387.8	2.25	0.79	-	-	-	34.66	0.29	1.25

Table 5. Participant's results and z- scores for anions in drinking water

Laboratory Code	F^-			PO_4^{-3}			Cl^-			NO_3^-			NO_2^-			SO_4^{-2}		
	Reference Value =0.914 mg/l			Refetence Value= =9.25 mg/l			Reference Value =27.1 mg/l			Reference Value= = 25.31 mg/l			Reference Value = =0.95 mg/l			Reference Value= =46.03 mg/l		
	σ = 0.148 mg/l			σ = 1.06 mg/l			σ = 2.64 mg/l			σ = 2.49 mg/l			σ = 0.15 mg/l			σ = 4.14 mg/l		
	x	s	z	x	s	z	x	s	z	x	s	z	x	s	z	x	s	z
1	0.926	0.036	0.11	9.21	0.30	-0.04	26.788	0.331	-0.12	26.26	0.331	0.38	0.931	0.036	-0.16	40.296	0.774	-1.39
2	0.86	0.01	-0.34	10.76	0.0608	1.42	28.41	0.03	0.50	27.24	0.06	0.78	0.963	0.004	0.05	52.23	0.112	1.50
3	-	-	-	6.45	0.7	**-2.65**	23.9	2.8	-1.21	28.7	0.80	1.36	1.017	0.039	0.40	63.4	9.3	**4.19**
4	0.75	0.1	-1.08	8.8	0.2	-0.43	27.2	0.7	0.04	26.98	0.80	0.67	0.74	0.05	-1.40	-	-	-
5	-	-	-	-	-	-	27.5	0.0	0.15	26.83	0.00	0.61	-	-	-	-	-	-
6	0.915	0.012	0.03	9.39	0.43	0.13	24.73	1.98	-0.90	24.89	0.43	-0.17	0.68	0.044	-1.80	47.27	0.61	0.30
7	0.584	0.021	**-2.20**	9.04	0.055	-0.20	27.0	0.1	0.03	27.34	0.28	0.82	0.96	0.013	0.03	47	0.38	0.23
8	1.193	0.046	1.19	-	-	-	32.1	0.29	-1.89	25.83	0.75	0.21	0.069	0.0019	**-5.79**	63.16	1.169	**4.14**
9	-	-	-	-	-	-	29.06	0.013	0.74	24.50	0.017	-0.50	0.947	0.0005	-0.05	-	-	-
10	-	-	-	-	-	-	31.2	0.478	1.55	22.96	0.543	-0.94	0.74	0.006	-1.4	-	-	-
11	-	-	-	-	-	-	29	0.25	0.72	28.7	0.65	1.36	0.76	0.03	-1.27	49	0.5	0.72
12	-	-	-	-	-	-	30	2.8	1.10	21.9	0.9	1.37	0.832	0.026	-0.80	-	-	-
13	-	-	-	-	-	-	29.8	2.0	1.02	28.5	0.002	1.28	0.81	0.002	-0.95	48	2	0.47
14	1.01	0.03	0.68	9.3	0.50	0.04	30.7	0.41	1.36	30.0	2.0	1.89	0.8	0.06	-1.01	45.0	2.0	-0.25
15	-	-	-	16.7	-	**7.03**	22.3	1.7	-1.82	25.3	0.055	0.00	0.15	0.0056	**-5.26**	84.4	0.369	**9.27**
17	-	-	-	-	-	-	35	0.018	**2.99**	43.19	0.22	**7.20**	0.8909	0.574	-0.42	81.94	0.4078	**8.67**
18	0.7	0.05	-1.42	8.3	0.06	-0.90	30.3	0.05	1.21	25.1	1.05	-0.08	0.75	0.03	-1.34	40	1.15	-1.46

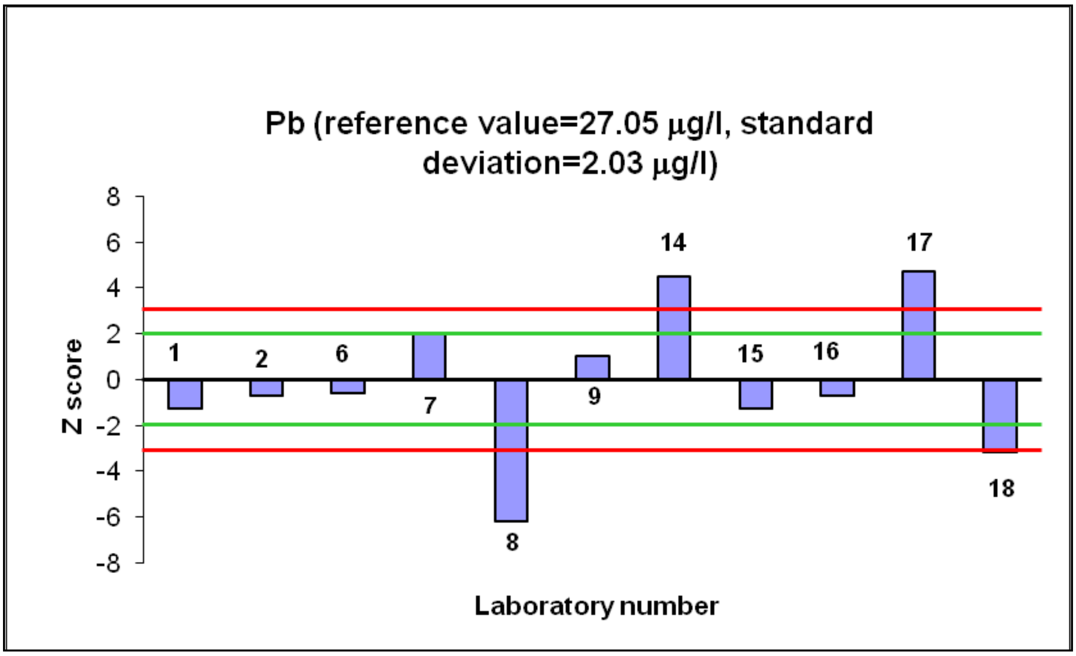

Figure 1. Z- Scores for Pb in drinking water

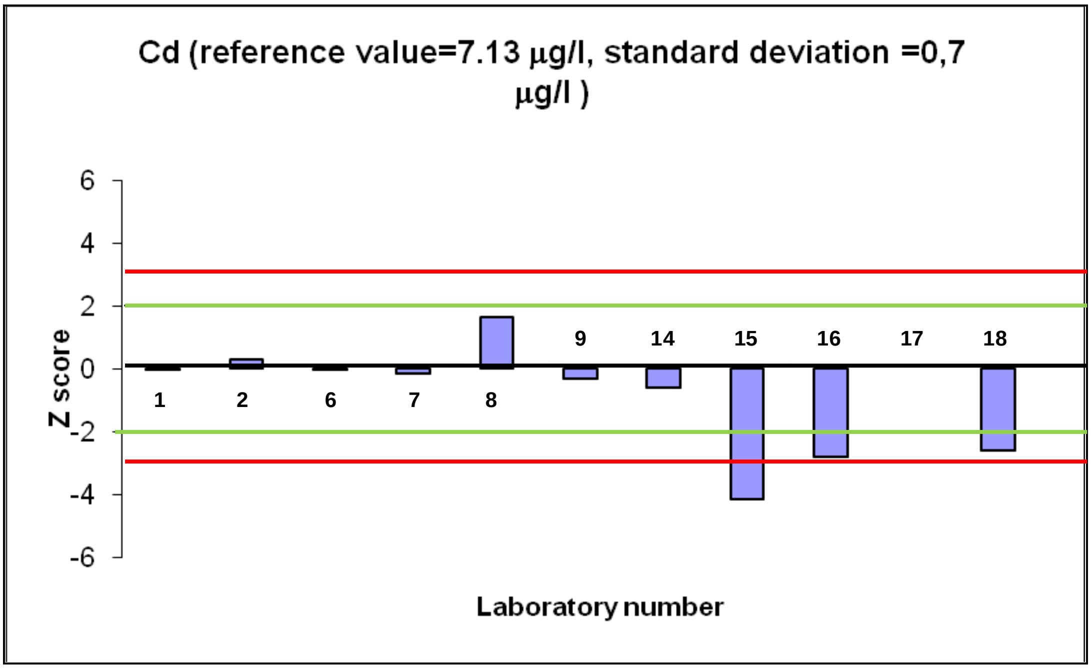

Figure 2. Z- Scores for Cd in drinking water

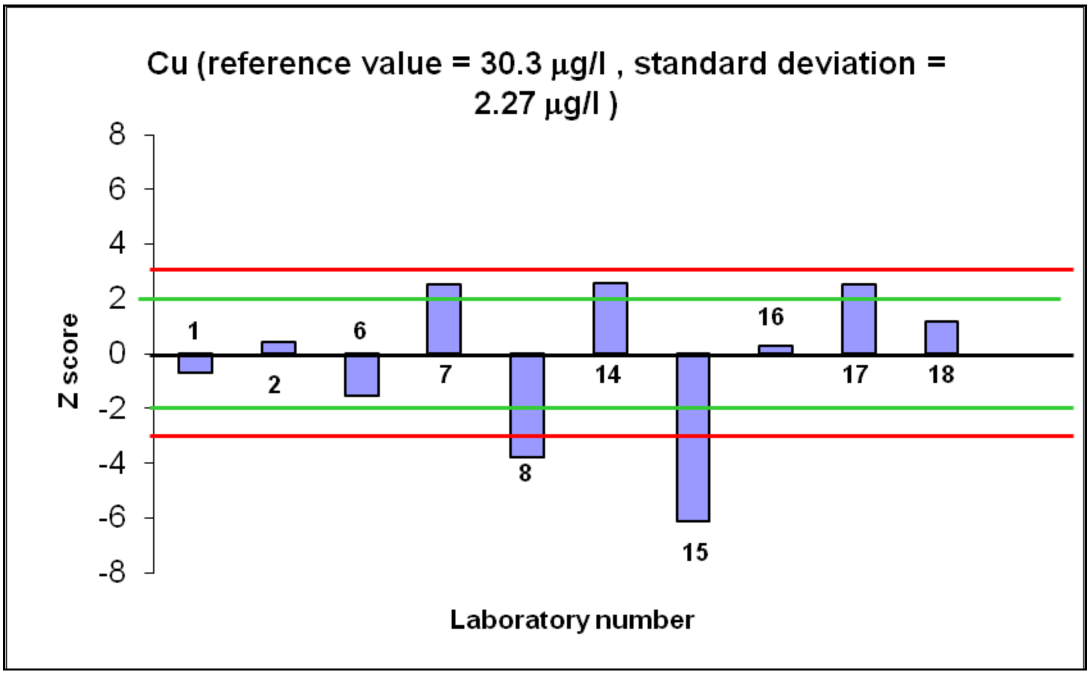

Figure 3. Z- Scores for Cu in drinking water

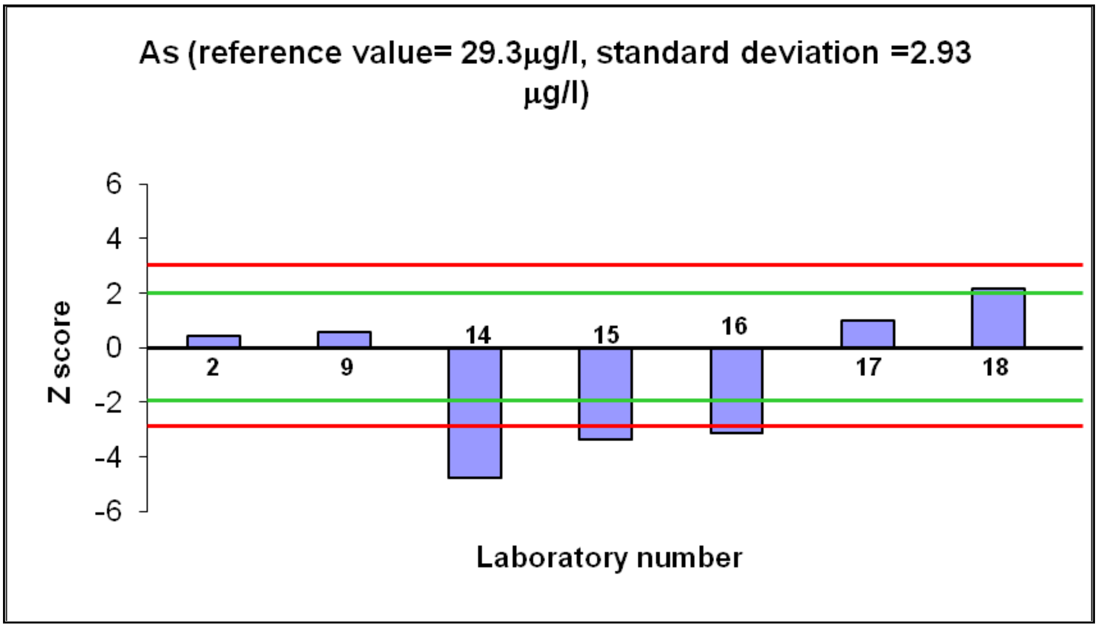

Figure 4. Z- Scores for As in drinking water

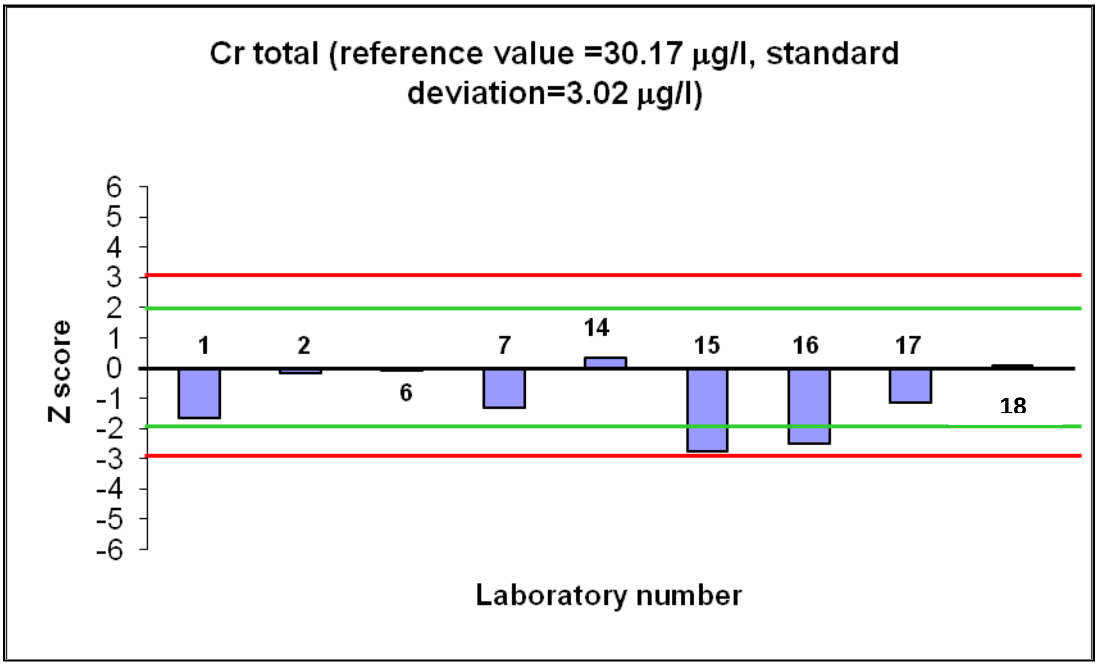

Figure 5. Z- Scores for Cr total in drinking water

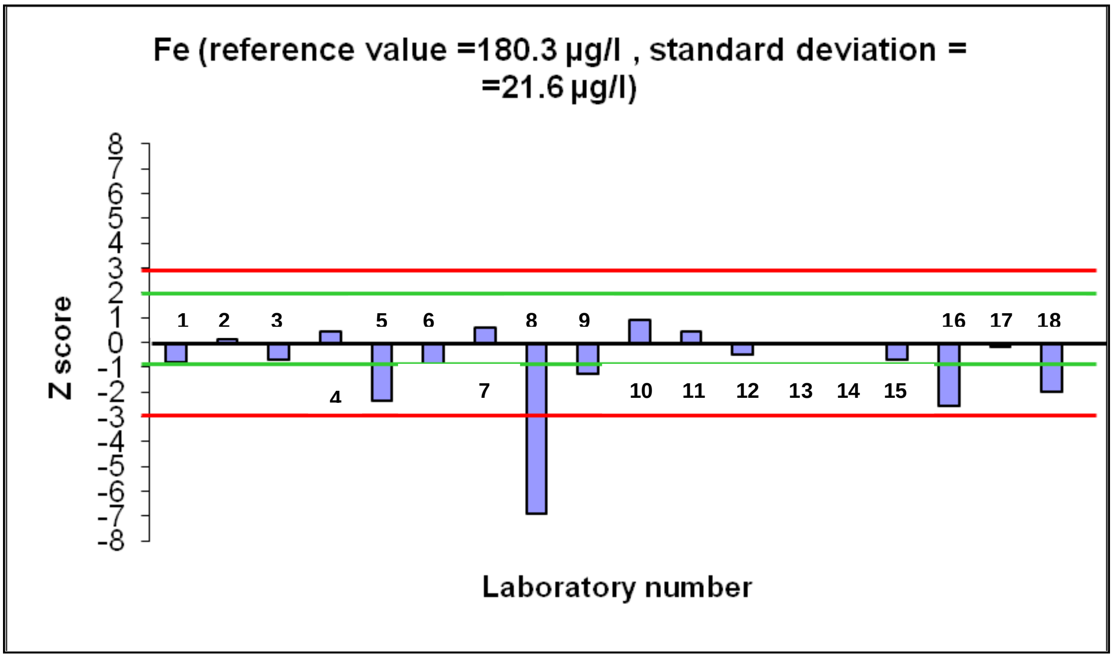

Figure 6. Z- Scores for Fe in drinking water

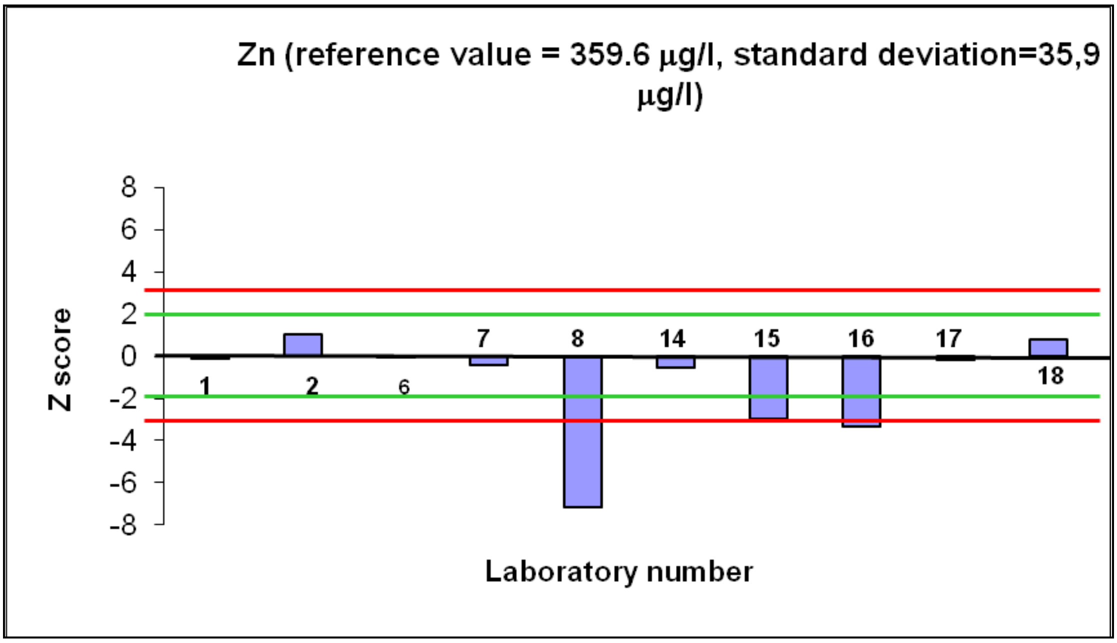

Figure 7. Z- Scores for Zn in drinking water

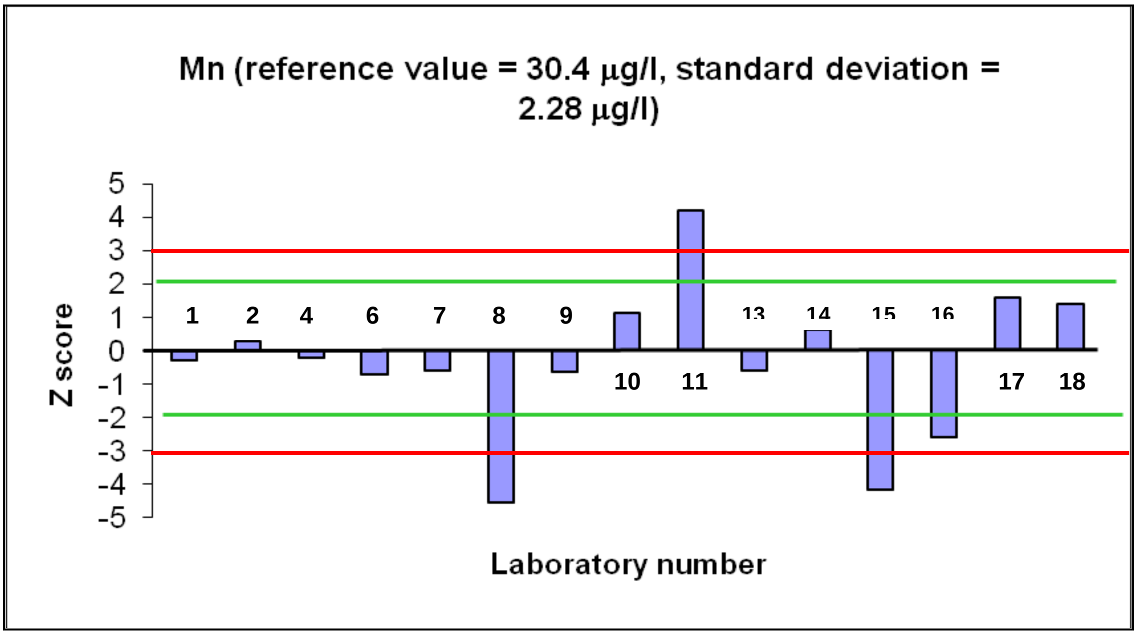

Figure 8. Z- Scores for Mn in drinking water

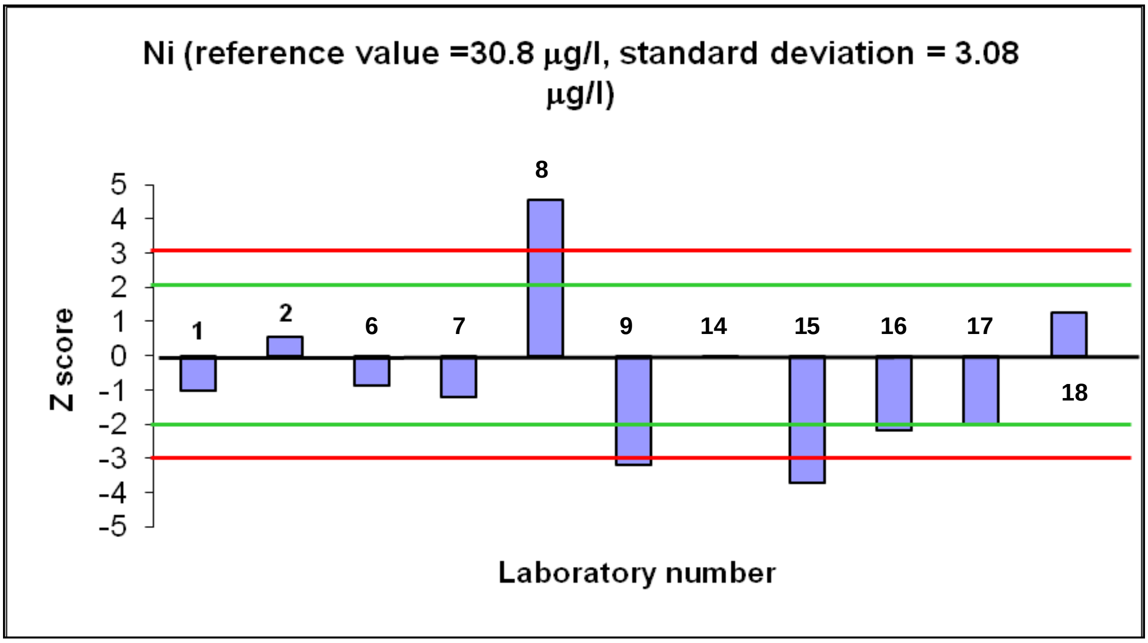

Figure 9. Z- Scores for Ni in drinking water

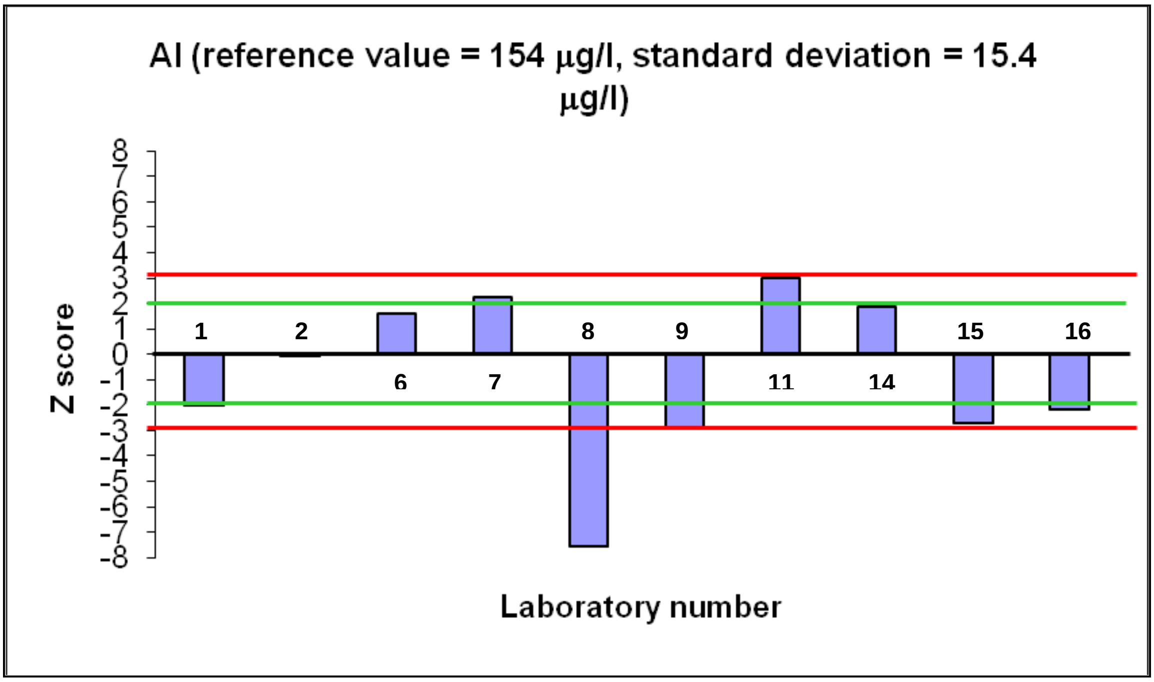

Figure 10. Z- Scores for Al in drinking water

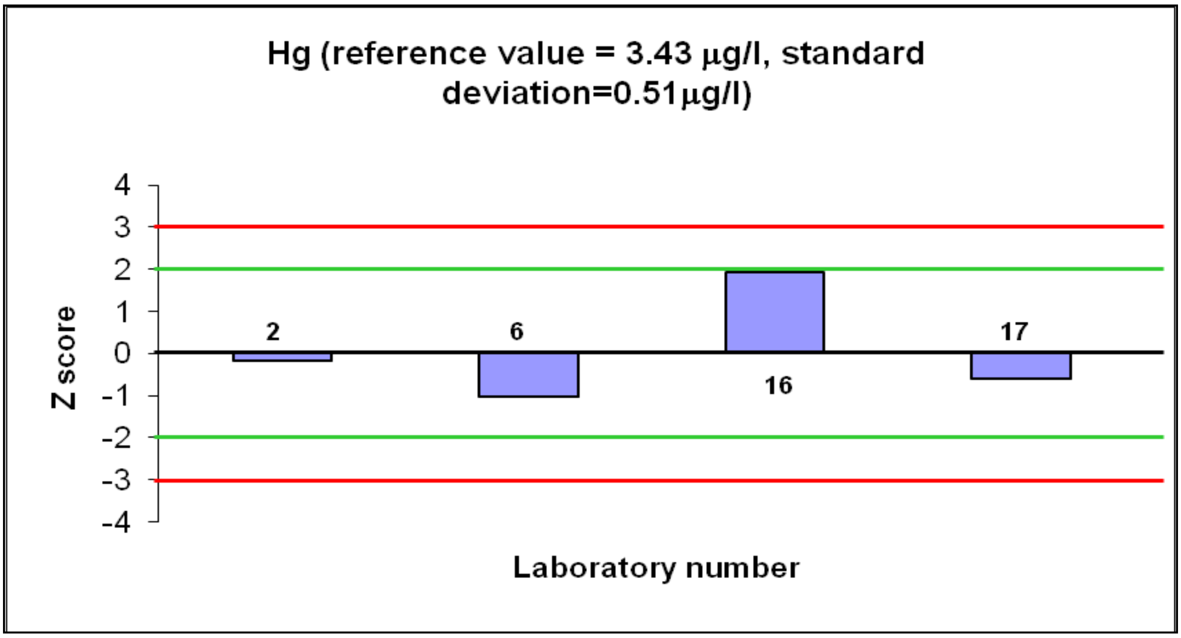

Figure 11. Z- Scores for Hg in drinking water

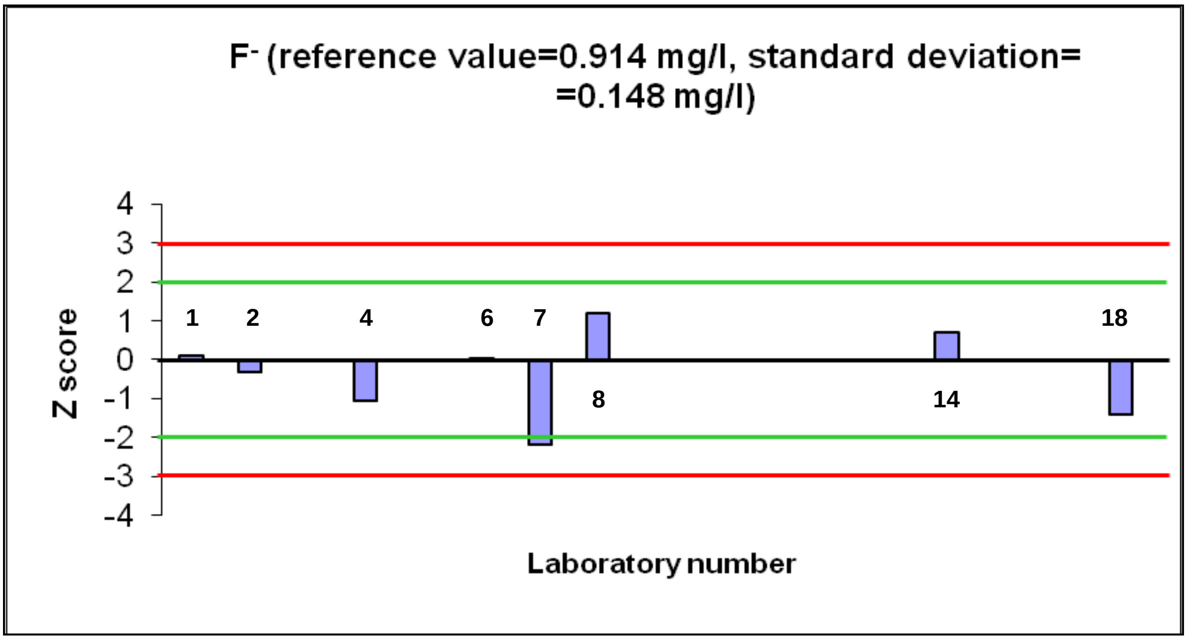

Figure 12. Z- Scores for F^- in drinking water

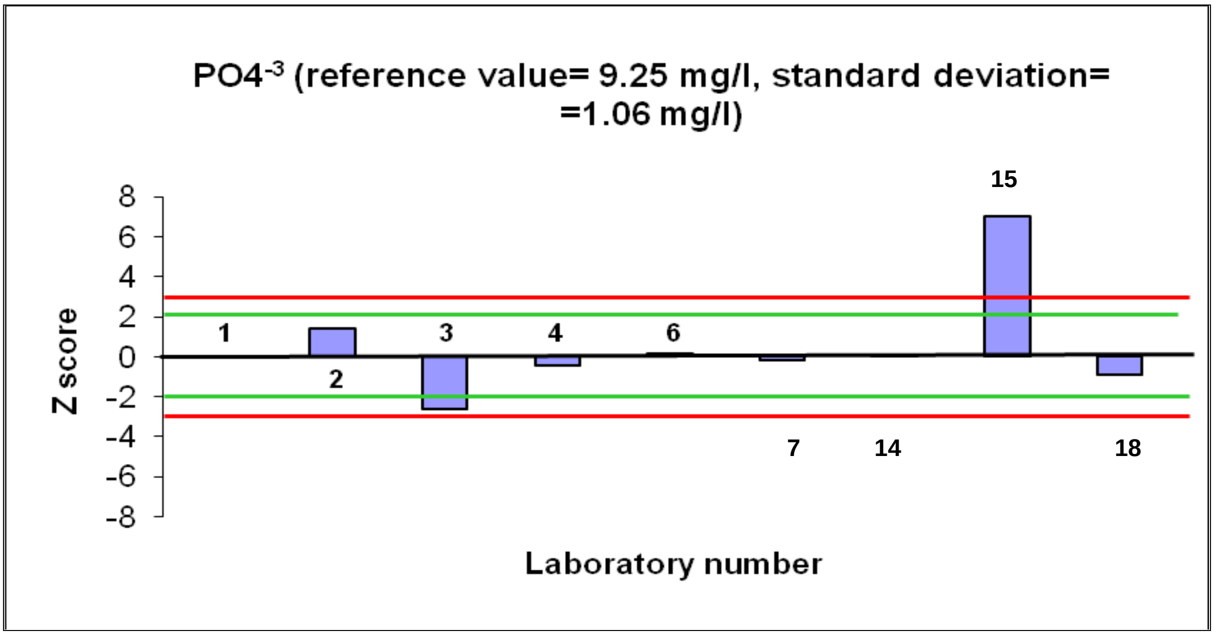

Figure 13. Z- Scores for PO_4^{-3} in drinking water

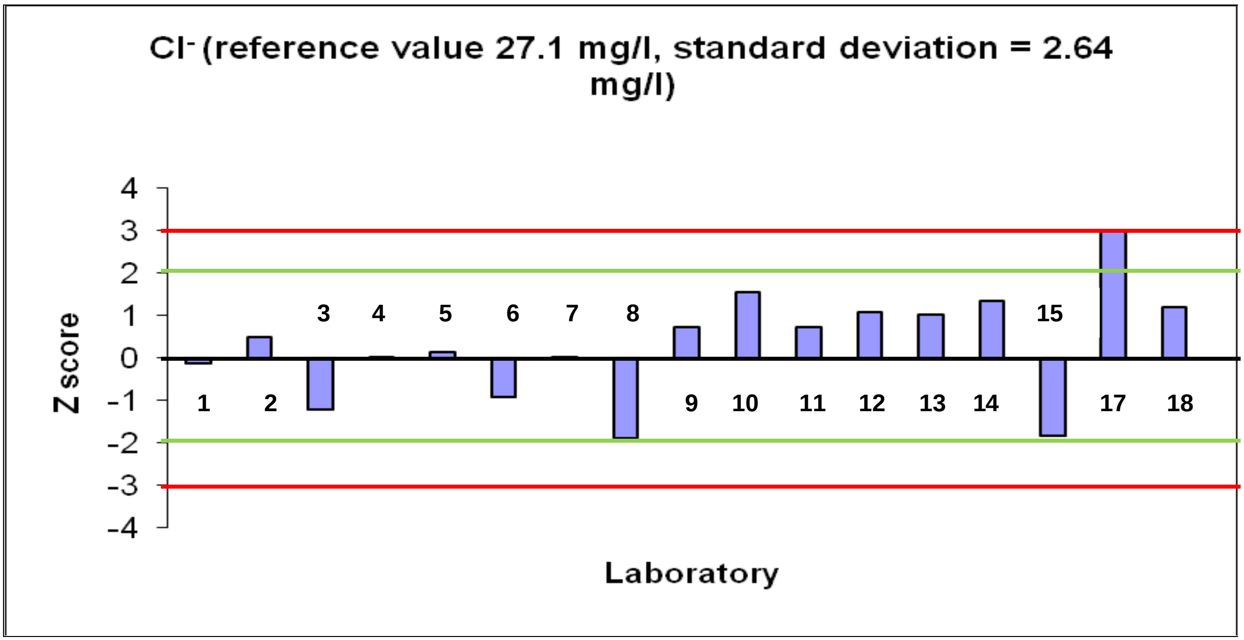

Figure 14. Z- Scores fo Cl^- in drinking water

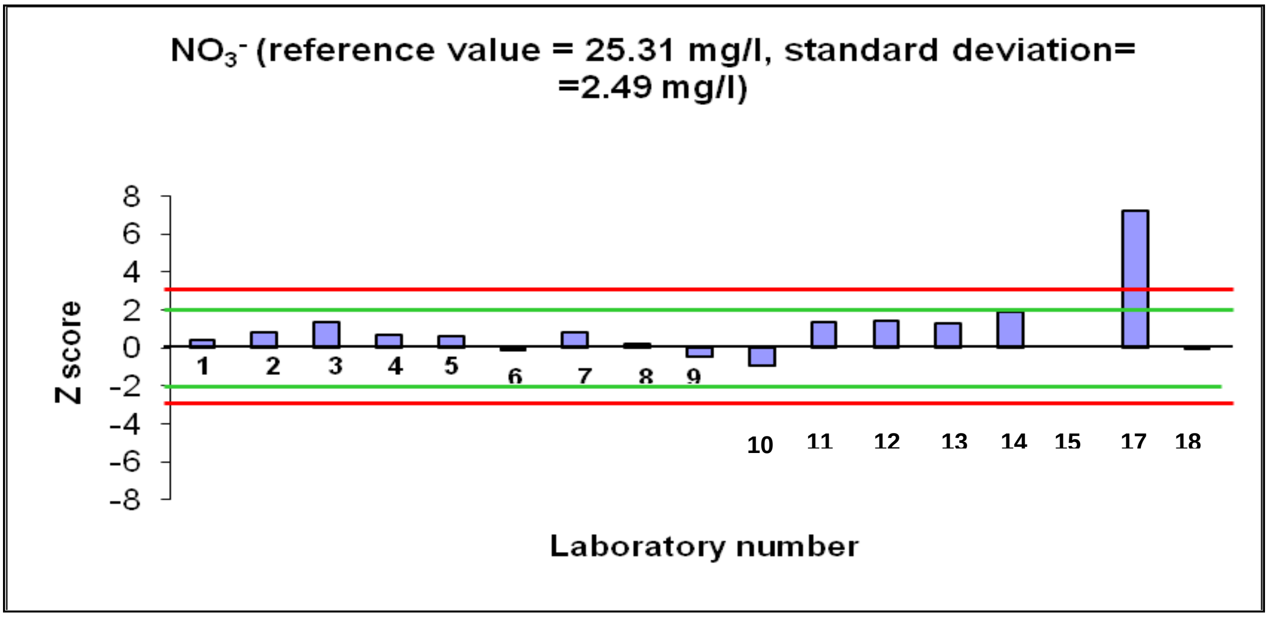

Figure 15. Z- Scores for NO_3^- in drinking water

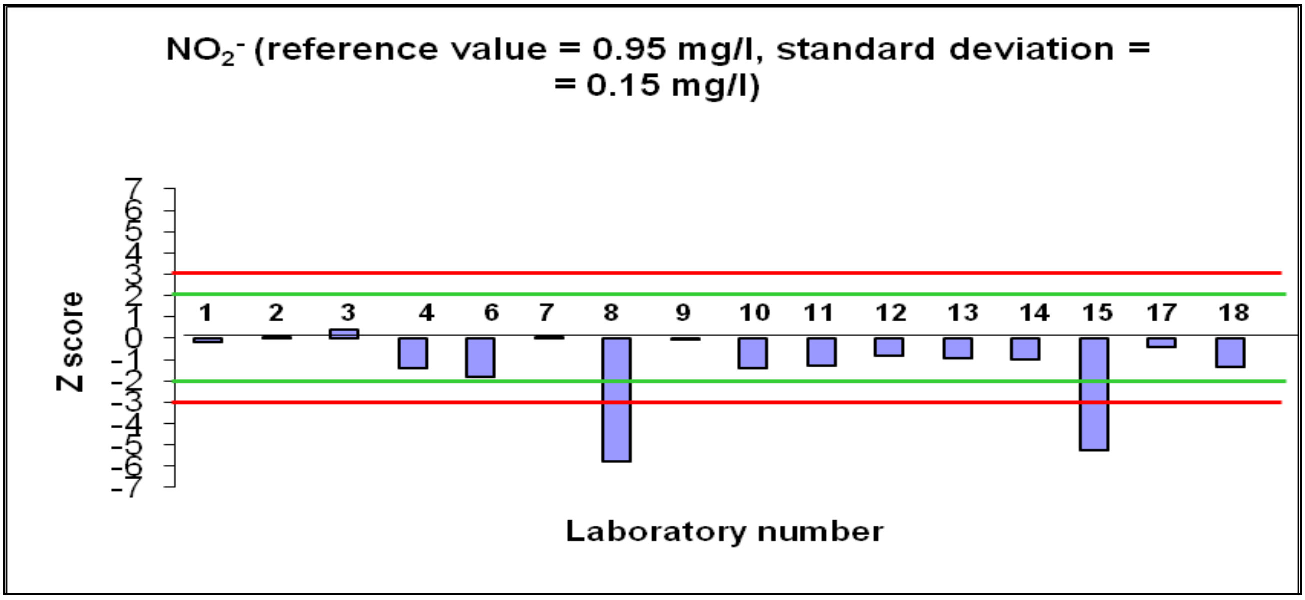

Figure 16. Z- Scores for NO_2 in drinking water

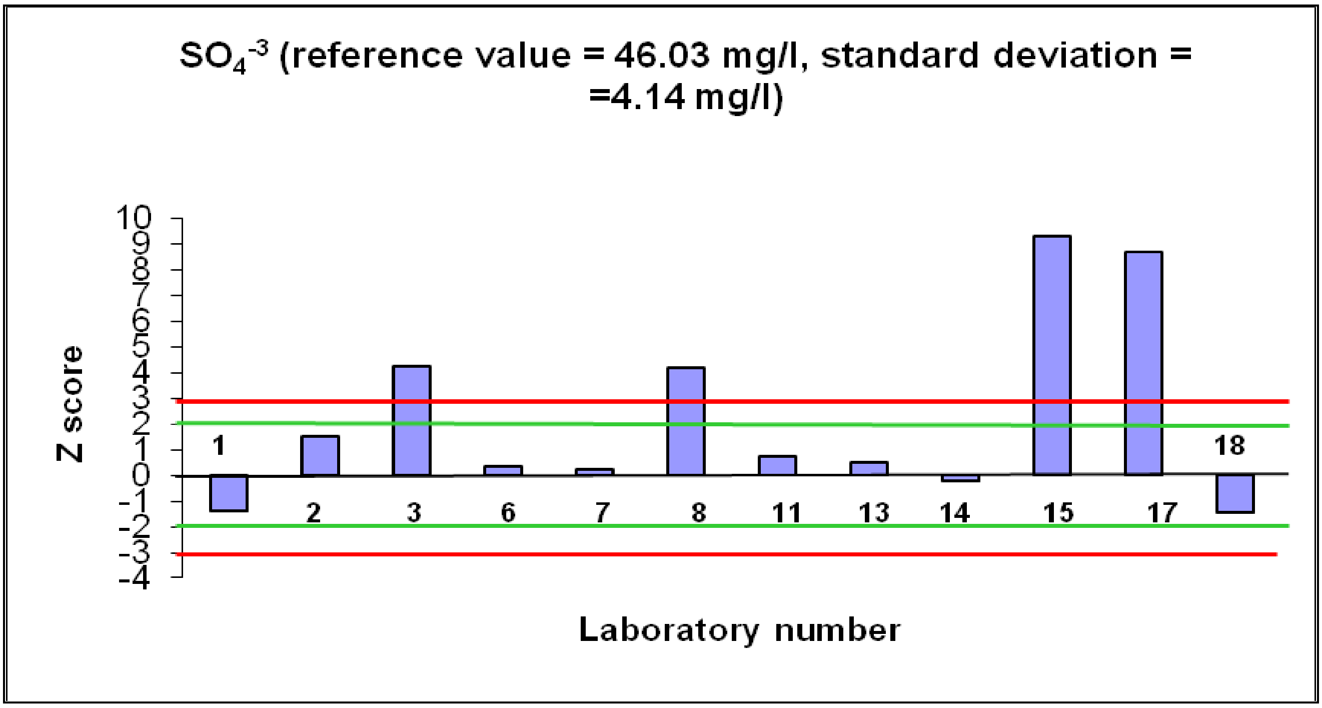

Figure 17. Z- Scores for SO_4^{-3} in drinking water

Table 6. Distribution of the z- scores for trace metals in drinking water

	$\lvert z\rvert \le 2.00$		$2.00 < \lvert z\rvert < 3.00$		$\lvert z\rvert \ge 3.00$		Total number of participants
	Number of participants	%	Number of participants	%	Number of participants	%	
Pb	7	64	-		4	36	11
Cd	9	82	2	18	1	9	11
Cu	5	50	3	30	2	20	10
Zn	7	70	1	10	2	20	10
Fe	14	78	3	16	1	5	18
Mn	11	69	1	6	3	19	16
Cr	6	60	2	20	-		10
As	3	43	1	14	3	43	7
Hg	4	100	-		-		4
Ni	6	55	2	18	3	27	11
Al	4	40	5	50	1	10	10

Table 7. Distribution of the z- scores for anions in drinking water

	$\lvert z\rvert \le 2.00$		$2.00 < \lvert z\rvert < 3.00$		$\lvert z\rvert \ge 3.00$		Total number of participants
	Number of participants	%	Number of participants	%	Number of participants	%	
F^-	7	87.5	-	-	1	12.5	8
PO_4^{-3}	7	77.8	1	11.1	1	11.1	9
Cl^-	16	94.1	1	5.9	-	-	17
NO_3^-	16	94.1	-	-	1	5.9	17
NO_2^-	14	87.5	-	-	2	12.5	16
SO_4^{-2}	8	66.7	-	-	4	33.3	12

Table 8. Distribution of the results for trace metals in drinking water

	Pb	Cd	Cu	Zn	Fe	Mn
Number of participants (n)	11	11	10	10	18	16
Median (µg/l)	22.53	6.21	30.85	341.5	167.5	22.88
Mean value (µg/l)	26.76	6.21	26.69	371.4	150.85	31.67
Reference value (µg/l l)	27.05	7.13	30.3	359.6	180.3	30.4
Standard deviation of the proficiency (µg/l)	2.03	0.7	2.27	35.9	21.6	2.28
Maximum value (µg/l)	36.55	8.26	36.2	396.3	200	40
Minimum value (µg/l)	14.46167	4.2	16.4	101.1	31	10
Range (Max/Min)	22	4	19.8	295.2	169	30

Table 8. Distribution of the results for trace metals in drinking water (continued)

	Cr	As	Hg	Ni	Al
Number of participants (n)	10	7	4	11	10
Median (µg/l l)	27.86	33.08	3.24	27.68	121.45
Mean value (µg/l)	27.86	26.32	3.24	31.17	140.23
Reference value (µg/l)	30.17	29.3	3.43	30.8	154
Standard deviation of the proficiency (µg/l)	3.02	2.93	0.51	3.08	15.4
Maximum value (µg/l l)	31.3	35.66	4.42	44.83333	200
Minimum value (µg/l)	21.9	15.25	3.129	19.3	36.333
Range (Max/Min)	9.4	20.4	1.29	25.5	163.6

Table 9. Distribution of the results for anions in drinking water

	F^-	PO_4^{-3}	Cl^-	NO_3^-	NO_2^-	SO_4^{-2}
Number of participants (n)	8	9	17	17	16	12
Median (mg/l)	0.89	9.77	29.00	26.83	0.80	48.50
Mean value (mg/l)	0.87	9.21	28.53	27.28	0.75	55.14
Reference value (mg/l)	0.914	9.25	27.1	25.30	0.95	46.03
Standard deviation of the proficiency (mg/l)	0.15	1.06	2.64	2.49	0.15	4.14
Maximum value (mg/l)	1.19	16.70	35	43.19	1.02	84.40
Minimum value (mg/l)	0.58	6.45	23.9	21.90	0.15	40.00
Range (Max/Min)	2.05	2.59	1.46	1.97	6.78	2.11

9. References

1. ISO/IEC 17043:2010, Conformity assessment – General Requirements for Proficiency Testing.
2. ISO 13258: 2005, Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons.
3. ISO/IEC 17025:2005, General Requirements for the Competence of Testing and Calibration Laboratories
4. Thompson, M., Ellison, S.R. and Wood, R., The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, Pure & Appl. ,Chem., 2006, Vol. 78, No. 1, pp. 145-196.
5. Guidance on the implementation of the Water Supply (Water Quality) Regulations 2000 (as amended) in England and the Water Supply (Water Quality) Regulations in Wales (Publishes September 2010).
6. William H., Evaluation of Analytical Methods Used for Regulations of Foods and Drugs, Analytical Chemistry, 1982 Vol. 54, No. 1, pp. 66-77.

10. APPENDIX A: Protocol distributed to participants

INSTITUTE OF PUBLIC HEALTH
SKOPJE, REPUBLIC OF MACEDONIA (FYROM)

PROFICIENCY TESTING SCHEME

PROTOCOL FOR DRINKING WATER

Protocol No: IPA 2011 PT 2

Novemver 2012

Vesna Kostik

REPUBLIC OF MACEDONIA, FYROM

INDEX

1. NATURE AND OBJECTIVE OF THE PROFICIENCY TESTING

Drinking water or potable water is water safe enough to be consumed by humans or used with low risk of immediate or long term harm. There are a variety of trace elements present all potable water, some of which play a role in metabolism. For example sodium, potassium and chloride are common chemicals found in small quantities in most waters, and these elements play a role in body metabolism. Other elements such as fluoride, while beneficial in low concentrations, can cause dental problems and other issues when present at high levels. Others such as lead, cadmium, mercury, arsenic, antimony, aluminum are considered toxic for humans. Therefore Maximum Allowed Values are set for trace elements, anions and other chemical and biological substances for drinking water.
Within the European program „Proficiency testing in IPA 2011" University of Ljubljana organized PRE-PT Training for laboratory comparison of testing and calibration laboratories in accordance with ILAC-G13, ISO Guide 43-1 and ISO 17043 for different testing scopes and for different testing items (11^{th} – 16^{th} June 2012).

The testing laboratory of Institute of Public Health of Republic of Macedonia (FYROM) was selected as the pilot laboratory for determination of trace elements and anions in drinking water.

2. ORGANIZATION AND DESIGN

Institute of Public Health of Republic of Macedonia (FYROM) is responsible for preparing and dispatching samples, performing homogeneity tests and assessment, conducting statistical analysis of data, collecting test results from all participating laboratories and sending final report to participants and participating accreditation bodies.

Organizer

Institution	Faculty of Electrical Engineering Laboratory of Metrology and Quality
Address	Tržaška 25 1000 Ljubljana, Slovenia
Phone	+386 1 4768 223, 224
Fax	+386 1 4264 633

Coordinator – Pilot Laboratory

Institution	Institute of Public Health, Skopje, Republic of Macedonia (FYROM)
Contact person	Vesna Kostić
Address	50 Divizija bb, PO Box 577 1000 Skopje, Republic of Macedonia (FYROM)
Phone	+3892 3226 510
Fax	+3892 3223 354
E-mail	vesna2mk@yahoo.com
Web	www.iph.mk

PT expert

Institution	TUBITAK UME
Contact person	Fatma AKÇADAĞ
Address	P.K. 54 41470 GEBZE-KOCAELI/TURKEY
Phone	+ 262 679 50 00
Fax	+ 262 679 50 01
E-mail	fatma.akcadag@tubitak.gov.tr

Participation to scheme

Proficiency Testing Scheme is open to the laboratories from Republic of Macedonia (FYROM) and Montenegro Supported by IPA 2011 project.

Test material

Natural spring water will be used in this PT scheme. The materials to be analyzed will be send in screwed two plastic bottles, each containing about 1000 ml of natural spring water spiked with trace elements: Pb (10-50) µg/l, Cd (1-10) µg/l, Hg (1-10) µg/l, As (10-50) µg/l, Ni (10-50) µg/l, Cr total (10-100) µg/l, Cu (10-200) µg/l, Fe (10 - 200) µg/l, Mn (10 - 50) µg/l, Al (10-200) µg/l and Zn (10 – 500) µg/l and anions: F^- (0.1- 2) mg/l, PO_4^{-3} (5-15) mg/l, Cl^- (10-100) mg/l, NO_3^- (10-100) mg/l, NO_2^- (0.1 – 1.5) mg/l and SO_4^{-2} (10-100) mg/l.

Sample preparation procedure for trace elements and anions is as follow, respectively:

Trace elements:

- Procurement of test material
- Washing the sample bottles with HNO_3
- Preparation of working standard solutions with CRM (50 -100 mL) (2 % HNO_3 for stabilization)
- Preparation of drinking water stock solution (1 L) (2 % HNO_3 for stabilization)
- Preparation of sample (20 or 30 L depending on the number of participants) (2 % HNO_3 for stabilization)
- Homogenisation of Sample (mixed for 2 - 4 h)
- Bottling of test material (1000 ml) and storing at 4 ^{o}C
- Homogeneity test
- Stability test

Anions:

- Procurement of test material
- Washing the sample bottles
- Preparation of drinking water stock solution (2 L)
- Preparation of sample (20 or 30 L depending on the number of participants)
- Homogenisation of Sample (mixed for 4-6 h)
- Bottling of test material (1000 ml) and storing at +4 ^{o}C
- Homogeneity test
- Stability test

The recommended storage temperature is +4 ^{0} C. All samples will be sent to participants at the same time by courier.

Participants are asked to check the contents of packages immediately on receipt and to contact coordinator if there are any problems with the condition of the test materials.

Framework of the scheme

The structure of scheme is as follows:

- Preparation, dispensing and quality control testing of test materials. October-November 2012
- Despatch of the test materials and instructions to participants. Each participating laboratory will receive the samples marked with laboratory code.

- The Protocol will be delivered through e-mail to each PT participating laboratory for drinking water, November 2012.

- Participants to analyse test materials and report results to Proficiency testing coordinator within the specified deadline.
- Results analysed and evaluation the performance of laboratories using appropriate techniques, such as z-scores.
  December 2012- April 2013
- Reports issued to participants,
  May 2013

ANALYSIS AND REPORTING OF RESULTS

Choice of methodology

Participants are free to use a method of their choice. It is recommended that to use same method and operator with routine analyses. Participants are asked to treat the PT materials in the same way as a routine sample. Participants may be asked to state their method when reporting results.

Reporting the results

It is recommended that results and calculations are checked thoroughly before reporting. Once submitted and received, results may only be amended at the discretion of the scheme coordinator. No changes can be made after the assigned values have been reported.

Participants are asked to report their results no later than 28/12/2012**.** Results should be report along with standard deviation of measurement and test method in the form given Appendix 1 of this Protocol in an electronic form (e-mail). The results registered with the signs < or > will not be processed.

After the deadline, the pilot laboratory reviews and processes the results. The reports with the results from the respective participating laboratories will be kept in confidentiality. In the final report, the participating laboratories will be marked with the code.

EVALUATION OF PERFORMANCE

Determination of the assigned value and standard deviation for proficiency testing

The assigned value is the value selected as being the best estimate of the "true value" for the parameter under test. The method used to determine the assigned value may vary depending upon the particular scheme and test material. When the assigned value is determined from the consensus value of participant results, robust statistical methods are used for the consensus value, the estimated standard uncertainty, and the robust standard deviation. The method used to derive them will be reported in the Scheme Report.

Once the assigned value for the parameters under test has been established, participant laboratories are assessed on the difference between their result and the assigned value. The assessment of the performance of the laboratories will be based on the z-scores. The advantages of a z-score are:

- Results can be expressed in a form that is relatively easy to interpret and understand
- Results can be summarised in graphical or tabular form to depict overall performance
- A performance score allows participants to directly compare their own result with others
- If consistent statistical values are applied, a performance score enables participants to monitor and trend their own performance over time

Z-scores

The participant's result, x, is converted into a z-score using the following formula;

$$z = \frac{x - X}{\sigma}$$

Where: X = assigned value

σ = standard deviation for proficiency testing assessment

For z-score the following interpretation is given to results.

$\lvert z \rvert \leq 2{,}00$	Satisfactory result
$2{,}00 < \lvert z \rvert < 3{,}00$	Questionable result
$\lvert z \rvert \geq 3{,}00$	Unsatisfactory result

REFERENCES

1. ISO/IEC 17043: 2010, Conformity assessment - General requirements for proficiency testing.
2. ISO/IEC 17025: 2005 General Requirements for the Competence of Testing and Calibration Laboratories, Thompson, M., Ellison, S.R. and Wood, R., The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, Pure & Appl. ,Chem., 2006, Vol. 78, No. 1, pp. 145-196.
3. ISO 13528 Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, 2005.
4. Thompson, M., Ellison, S.R. and Wood, R., The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, Pure & Appl. ,Chem., 2006, Vol. 78, No. 1, pp. 145-196.
5. Mercury Preservation Techniques, EPA, 2003.
6. ISO/IEC: 15586:2003.

APPENDIX 1: IPA 2011 - PT 2 – Drinking Water
REPORT FORM

FROM:

Laboratory Code

TO: Vesna Kostik
Institute of Public Health, street " 50 Divizija" No. 6, 1000 Skopje,
Republic of Macedonia (FYROM); phone: + 3892 3226 510 (122); fax: + 3892 3223 354

Parameter	Result	Standard Deviation	Unit	Test Method	Date of Analysis
Al			µg/L		
As			µg/L		
Cd			µg/L		
Cr			µg/L		
Cu			µg/L		
Fe			µg/L		
Hg			µg/L		
Ni			µg/L		
Pb			µg/L		
Mn			µg/L		
Zn			µg/L		
F^-			mg/L		
PO_4^{-3}			mg/L		
Cl^-			mg/L		
NO_3^-			mg/L		
NO_2^-			mg/L		
SO_4^{-2}			mg/L		
Name			**Signature**		**Date**

APPENDIX 2: IPA 2011 - PT 2 – Drinking Water Sample Receipt Form

Laboratory name		
Responsible Person		
Address		
Country		
Phone:	Fax:	
e-mail:		

Sample	√	Remark
Drinking water (trace elements)		
Drinking water (anion)		

Please tick "√" indicating that you have received the PT samples. If there are any problems with the PT samples note in the "Remark" column

I confirm that samples have been received by the laboratory.	Received by	Date	Signature

Please return the Sample Receipt Form by e-mail to the scheme coordinator Vesna Kostik.

e-mail:vesna2mk@yahoo.com

11. APENDIX B: SAMPLE PREPARATION, HOMOGENEITY and STABILITY

11.1 Sample Preparation

Natural spring water was used in the preparation of the test material. For trace element's (metal) analysis natural spring water was spiked with appropriate quantities of CRM (ICP Multi-element standard solution) and single standard stock solutions. CRM solution used for spiking contained following elements: Al (500) mg/l, As (100) mg/l, Cd (25) mg/l, Cr (100) mg/l, Cu (100) mg/l, Mn (100) mg/l, Ni (100) mg/l and Pb (100) mg/l. Single standard solutions contained: Hg (1000) mg/l, Fe (1000) mg/l and Zn (1000) mg/l respectively.

Preparation of the test samples was as follows:

- Preparation of working standard solutions
- Preparation of drinking water stock solution 1l (stabilization with HNO_3)
- Preparation of the sample (20 l and stabilization with HNO_3 to between pH 1 to 2)
- Homogenization of the sample – mixing for approximately 4 hours
- Bottling of PT test samples (1 l) in polyethylene bottles (PET) and labeling
- Storage at + 4^0 C

Final concentration of trace elements in test samples was: Pb (10-50) µg/l, Cd (1-10) µg/l, Hg (1-10) µg/l, As (10-50) µg/l, Ni (10-50) µg/l, Cr total (10-100) µg/l, Cu (10-200) µg/l, Fe (10-200) µg/l, Mn (10-50) µg/l, Al (10-200) µg/l and Zn (10 – 500) µg/l.

For anion analysis natural spring water was spiked with appropriate quantities of single standard stock solutions: F^- (1000) mg/l, Cl^- (1000) mg/l, PO_4^{-3} (1000) mg/l, NO_3^- (1000) mg/l, NO_2^- (1000) mg/l and SO_4^{-3} (1000) mg/l respectively.

Preparation of the test samples was as follows:

- Preparation of working standard solutions
- Preparation of drinking water stock solution
- Preparation of the sample (20 l)
- Homogenization of the sample – mixing for approximately 4 hours
- Bottling of PT test samples (1 l) in polyethylene bottles (PET) and labelling
- Storage at + 4^0 C

Final concentration of anions in test samples was: F^- (0.1- 2) mg/l, PO_4^{-3} (5 -15) mg/l, Cl^- (10-100) mg/l, NO_3^-, (10 -100) mg/l, NO_2^- (0.1– 1.5) mg/l and SO_4^{-2} (10 -100) mg/l.

11.2. Homogeneity

Ten bottles were analyzed in duplicate in order to assess the homogeneity of the samples for metals and anions. Metal analysis was carried out by ETAAS (Pb, Cd, Ni, Al, Cu, Cr and Mn); FIMS (Hg); FAAS (Fe and Zn) and FIAS (As). Analysis of anions was carried out by ion chromatography (IC). For the homogeneity test the results were evaluated by using below equations according to the method ISO 13259.

$\mathbf{X}_{t,k}$

Where:
t: represents the sample (t = 1,2…….g)

k: represents the test portion (k = 1, 2)

$$t,. = \frac{(x_{t,1} + x_{t,2})}{2} \qquad w_t = |x_{t,1} - x_{t,2}| \qquad \bar{x}_{.,.} = \Sigma\, \bar{x}_{.,.}/g$$

$$Sx = \sqrt{\Sigma\, (x_{t,.} - x_{.,.})^2 / (g-1)} \qquad S_w = \sqrt{\Sigma\, w_t^2 / (2g)} \qquad S_S = \sqrt{S_X^2 - (S_W^2/2)}$$

Where:

$\bar{x}_{tv}$: samples averages

$\mathbf{w_t}$ **:** between "test " portion range

$\bar{x}_{.v}$: general average of the result obtained in the homogeneity stability check

s_X: standard deviation of sample averages

s_W: within samples standard deviation

s_s: between – samples standard deviation

Compare the between – samples standard deviation $s_{s,}$ with the standard deviation for proficiency assessment σ. The samples may be considered to be adequately homogenous if:

$$S_S \leq 0.3\ \sigma$$

The results of homogeneity study are shown in Table 12 – Table 18. It was concluded that there was not a significant difference between the bottles. As a conclusion, this material is suitable for proficiency testing.

Table 10. Homogeneity results for Pb, Cd and Cr total

Pb						Cd						Cr					
t	***v***					**t**	***v***					**t**	***v***				
	1	**2**	$\mathbf{X_{t,v}}$	$\mathbf{w_t}$	$\mathbf{w_t^2}$		**1**	**2**	$\mathbf{X_{t,v}}$	$\mathbf{w_t}$	$\mathbf{w_t^2}$		**1**	**2**	$\mathbf{X_{t,v}}$	$\mathbf{w_t}$	$\mathbf{w_t^2}$
1	26.94	26.87	26.90	0.07	0.0049	1	7.41	7.51	7.46	0.10	0.01	1	30.35	30.88	30.61	0.53	0.2809
2	27.33	27.22	27.27	0.11	0.0121	2	7.34	7.46	7.40	0.12	0.0144	2	30.19	30.27	30.23	0.08	0.0064
3	26.98	27.07	27.02	0.09	0.0081	3	7.43	7.51	7.47	0.08	0.0064	3	30.28	29.79	30.03	0.49	0.2401
4	27.11	27.13	27.12	0.02	0.0004	4	7.38	7.39	7.385	0.01	0.0001	4	29.89	30.16	30.02	0.27	0.0729
5	27.08	26.94	27.01	0.14	0.0196	5	7.65	7.44	7.54	0.21	0.0441	5	29.78	30.11	29.78	0.33	0.1089
6	26.89	26.79	26.84	0.10	0.0100	6	7.44	7.61	7.52	0.17	0.0289	6	30.08	29.93	30.01	0.15	0.0225
7	27.17	27.23	27.2	0.06	0.0036	7	7.50	7.55	7.52	0.05	0.0025	7	29.94	29.21	29.57	0.73	0.5329
8	26.95	27.11	27.03	0.16	0.0256	8	7.52	7.48	7.50	0.04	0.0016	8	30.66	30.54	30.60	0.12	0.0144
9	27.03	26.84	26.93	0.19	0.0361	9	7.38	7.51	7.44	0.13	0.0169	9	30.49	30.81	30.65	0.32	0.1024
10	27.0	26.79	26.89	0.21	0.0441	10	7.59	7.50	7.54	0.09	0.0810	10	29.83	29.69	29.76	0.14	0.0196
		X_v	27.02					X_v	7.45					X_v	30.02		
		S_x	0.058					S_x	0.03					S_x	0.134		
		S_w	0.091					S_w	0.067					S_w	0.265		
		S_s	0.027					S_s	0.037					S_s	0.129		
		σ	2.03					σ	0.7					σ	3.02		
		0.3σ	0.61					0.3σ	0.21					0.3σ	0.906		
		0.027	<	0.61				0.037	<	0.21				0.129	<	0.906	

Table 11. Homogeneity results for As, Hg and Cu

As					
t	***v***				
	1	**2**	**$X_{t,v}$**	**w_t**	**w_t^2**
1	28.80	28.78	27.79	0.02	0.0004
2	28.67	28.92	28.79	0.25	0.0625
3	28.87	28.69	28.78	0.18	0.0324
4	28.79	28.71	28.75	0.08	0.0064
5	28.90	28.85	28.87	0.05	0.0025
6	28.57	28.69	28.63	0.12	0.0144
7	28.77	28.74	28.75	0.03	0.0009
8	28.81	28.76	28.78	0.05	0.0025
9	28.80	28.80	28.80	0	0
10	28.9	28.77	28.83	0.13	0.169
		X_v	28.80		
		S_x	0.002		
		S_w	0.083		
		S_s	0.045		
		σ	2.93		
		0.3σ	0.879		
		0.045	<	0.879	

Hg					
t	***v***				
	1	**2**	**$X_{t,v}$**	**w_t**	**w_t^2**
1	3.49	3.51	3.50	0.02	0.0004
2	3.50	3.48	3.49	0.02	0.0004
3	3.54	3.53	3.53	0.01	0.001
4	3.48	3.43	3.45	0.05	0.0025
5	3.51	3.44	3.47	0.07	0.0049
6	3.43	3.49	3.46	0.06	0.0036
7	3.44	3.38	3.41	0.06	0.0036
8	3.39	3.42	3.40	0.03	0.0009
9	3.51	3.51	3.51	0	0
10	3.53	3.55	3.54	0.02	0.0004
		X_v	3.52		
		S_x	0.233		
		S_w	0.029		
		S_s	0.134		
		σ	0.51		
		0.3σ	0.153		
		0.134	<	0.153	

Cu					
t	***v***				
	1	**2**	**$X_{t,v}$**	**w_t**	**w_t^2**
1	29.49	29.47	29.48	0.02	0.0004
2	29.51	29.38	29.44	0.13	0.0169
3	29.68	29.67	29.67	0.01	0.0001
4	29.55	29.53	29.54	0.02	0.0004
5	29.61	29.44	29.52	0.17	0.0289
6	29.48	29.47	29.47	0.01	0.0001
7	29.62	29.39	29.50	0.23	0.0529
8	29.55	29.56	29.54	0.01	0.0001
9	29.60	29.43	29.51	0.17	0.0289
10	29.47	29.50	29.48	0.03	0.0009
		X_v	29.52		
		S_x	0.013		
		S_w	0.12		
		S_s	0.08		
		σ	2.27		
		0.3σ	0.681		
		0.08	<	0.681	

Table 12. Homogeneity results for Ni, Fe and Mn

Ni					
t	***v***				
	1	**2**	**$X_{t,v}$**	**w_t**	**w_t^2**
1	29.55	29.49	29.52	0.06	0.0036
2	29.48	29.51	29.49	0.03	0.0009
3	29.64	29.63	29.63	0.01	0.0001
4	29.59	29.64	29.61	0.05	0.0025
5	29.60	29.54	29.57	0.06	0.0036
6	29.70	29.55	29.62	0.15	0.0225
7	29.57	29.47	29.52	0.10	0.01
8	29.55	29.60	29.57	0.05	0.0025
9	29.71	29.80	29.75	0.09	0.0081
10	29.49	29.64	29.56	0.15	0.0225
		X_v	29.59		
		S_x	0.252		
		S_w	0.036		
		S_s	0.251		
		σ	3.08		
		0.3σ	0.924		
		0.251	<	0.924	

Fe					
t	***v***				
	1	**2**	**$X_{t,v}$**	**w_t**	**w_t^2**
1	180.2	180.1	180.2	0.13	0.0169
2	179.8	179.6	179.7	0.19	0.0361
3	179.7	180.2	179.9	0.50	0.2500
4	180.1	180.1	180.1	0.04	0.0016
5	179.5	179.9	179.7	0.34	0.1156
6	181	180.9	180.9	0.10	0.01
7	180.1	179.4	179.8	0.63	0.3969
8	180.1	180.6	180.4	0.51	0.2601
9	180.2	180.1	180.2	0.09	0.0081
10	180.7	181.1	180.9	0.38	0.1444
		X_v	180.6		
		S_x	0.671		
		S_w	0.249		
		S_s	0.648		
		σ	21.6		
		0.3σ	6.48		
		0.648	<	6.48	

Mn					
t	***v***				
	1	**2**	**$X_{t,v}$**	**w_t**	**w_t^2**
1	30.42	30.55	30.48	0.13	0.0169
2	30.21	30.41	30.31	0.2	0.04
3	30.08	30.57	30.32	0.49	0.2401
4	60.54	30.66	30.6	0.12	0.0144
5	30.6	30.22	30.41	0.38	0.0144
6	31	29.84	30.42	1.16	1.3456
7	30.55	29.8	30.17	0.75	0.5625
8	30.48	30.1	30.29	0.38	0.1444
9	30.72	30.33	30.52	0.39	0.1521
10	29.88	30.65	30.26	0.77	0.5929
		X_v	30.53		
		S_x	0.431		
		S_w	0.386		
		S_s	0.334		
		σ	2.28		
		0.3σ	0.684		
		0.334	<	0.684	

Table 13. Homogeneity results for Al and Zn

Al						Zn					
t	***v***					**t**	***v***				
	1	**2**	$\mathbf{X_{t,v}}$	$\mathbf{w_t}$	$\mathbf{w_t^2}$		**1**	**2**	$\mathbf{X_{t,v}}$	$\mathbf{w_t}$	$\mathbf{w_t^2}$
1	155.6	155.8	155.7	0.2	0.04	1	360.1	360.2	360.1	0.1	0.01
2	155.8	155.6	155.7	0.2	0.04	2	359.8	359.8	359.8	0	0
3	155.7	155.6	155.6	0.1	0.01	3	361	360.6	360.8	0.4	0.16
4	155.5	155	155.2	0.5	0.25	4	360.8	359.6	360.2	1.25	1.5625
5	155.9	155.6	155.7	0.3	0.09	5	360.2	359.2	359.7	1	1
6	156	155.7	155.8	0.7	0.49	6	359.7	360	359.8	0.3	0.09
7	154.8	155	154.9	0.8	0.64	7	358.8	359.7	359.2	0.9	0.81
8	155	154.8	154.9	0.8	0.64	8	361	360.2	360.6	0.8	0.64
9	155.9	154.7	155.3	0.2	0.04	9	360.6	360	360.3	0.6	0.36
10	155.7	155.3	155.5	0.4	0.16	10	360	360.1	360.0	0.08	0.0064
		X_v	155.4					X_v	360.1		
		S_x	0.347					S_x	0.451		
		S_w	0.346					S_w	0.482		
		S_s	0.246					S_s	0.296		
		σ	15.4					σ	35.9		
		0.3σ	4.62					0.3σ	10.8		
		0.246	<	4.62				0.296	<	10.8	

Table 14. Homogeneity results for F^-, Cl^- and PO_4^{-3}

F^-						PO_4^{-3}						Cl^-					
t	***v***					**t**	***v***					**t**	***v***				
	1	**2**	$X_{t,v}$	w_t	w_t^2		**1**	**2**	$X_{t,v}$	w_t	w_t^2		**1**	**2**	$X_{t,v}$	w_t	w_t^2
1	0.915	0.92	0.918	0.005	0.000025	1	9.20	9.32	9.26	0.12	0.014	1	27.01	27.11	27.06	0.10	0.01
2	0.890	0.915	0.903	0.025	0.000625	2	9.34	9.22	9.28	0.12	0.014	2	27.12	27.22	27.17	0.10	0.01
3	0.923	0.920	0.922	0.0030	0.000009	3	9.53	9.46	9.49	0.07	0.005	3	27.00	27.15	27.07	0.15	0.0225
4	0.936	0.920	0.928	0.0160	0.000256	4	9.65	9.06	9.35	0.59	0.3500	4	26.89	27.00	26.94	0.11	0.0121
5	0.878	0.890	0.884	0.0120	0.000144	5	9.43	9.15	9.29	0.28	0.0784	5	27.12	26.98	27.05	0.14	0.0196
6	0.918	0.932	0.925	0.0140	0.000196	6	9.78	9.34	9.56	0.44	0.1936	6	26.93	27.00	26.96	0.07	0.0049
7	0.890	0.91	0.901	0.0210	0.000441	7	9.67	9.70	9.68	0.03	0.0009	7	27.30	27.07	27.18	0.23	0.0529
8	0.915	0.922	0.919	0.0070	0.000049	8	9.23	9.34	9.28	0.11	0.0121	8	27.10	27.23	27.16	0.13	0.0169
9	0.920	0.912	0.916	0.0080	0.000064	9	9.13	9.20	9.16	0.07	0.0049	9	27.34	27.29	27.31	0.05	0.0025
10	0.900	0.91	0.905	0.0100	0.0001	10	9.44	9.15	9.29	0.29	0.0841	10	27.40	26.99	27.19	0.09	0.0081
		X_v	0.912					X_v	9.37					X_v	27.1		
		S_x	0.014					S_x	0.16					S_x	0.114		
		S_w	0.010					S_w	0.19					S_w	0.089		
		S_s	0.012					S_s	0.088					S_s	0.095		
		σ	0.148					σ	1.06					σ	2.64		
		0.3σ	0.044					0.3σ	0.318					0.3σ	0.792		
		0.012	<	0.044				0.088	<	0.318				0.095	<	0.792	

Table 15. Homogeneity results for NO_3^- , NO_2^- and SO_4^{-2}

NO_3^-					
t	***v***				
	1	**2**	$\mathbf{X_{t,v}}$	$\mathbf{w_t}$	$\mathbf{w_t^2}$
1	25.31	25.17	25.24	0.14	0.0196
2	25.67	25.66	25.66	0.01	0.0001
3	25.72	25.65	25.68	0.07	0.0049
4	25.48	25.78	25.63	0.30	0.0900
5	25.27	25.19	25.23	0.08	0.0064
6	25.55	25.45	25.50	0.10	0.0100
7	25.70	25.78	25.74	0.08	0.0064
8	25.87	25.45	25.66	0.42	0.1764
9	25.56	25.71	25.63	0.15	0.0225
10	25.97	26.01	25.99	0.04	0.0016
		X_v	25.58		
		S_x	0.23		
		S_w	0.13		
		S_s	0.21		
		σ	2.49		
		0.3σ	0.75		
		0.21	<	0.75	

NO_2^-					
t	***v***				
	1	**2**	$\mathbf{X_{t,v}}$	$\mathbf{w_t}$	$\mathbf{w_t^2}$
1	0.971	0.969	0.970	0.002	0.000004
2	0.982	0.985	0.983	0.003	0.000009
3	0.968	0.975	0.971	0.007	0.000049
4	0.974	0.968	0.971	0.006	0.000036
5	0.963	0.970	0.966	0.007	0.000049
6	0.975	0.970	0.972	0.005	0.000025
7	0.972	0.976	0.974	0.004	0.000016
8	0.990	0.980	0.985	0.010	0.00010
9	0.985	0.992	0.988	0.007	0.000049
10	0.978	0.973	0.975	0.007	0.000049
		X_v	0.976		
		S_x	0.0073		
		S_w	0.0044		
		S_s	0.0066		
		σ	0.15		
		0.3σ	0.047		
		0.0066	<	0.047	

SO_4^{-2}					
t	***v***				
	1	**2**	$\mathbf{X_{t,v}}$	$\mathbf{w_t}$	$\mathbf{w_t^2}$
1	46.12	46.25	46.185	0.13	0.0169
2	46.18	46.10	46.140	0.08	0.0064
3	45.97	46.18	46.075	0.21	0.0441
4	45.89	45.98	45.935	0.09	0.0081
5	46.18	46.23	46.205	0.05	0.0025
6	45.90	45.99	45.945	0.09	0.0081
7	46.22	46,26	46.240	0.04	0.0016
8	46.09	46.19	46.140	0.10	0.0100
9	46.23	46.30	46.265	0.07	0.0049
10	46.10	46.22	46.160	0.12	0.0144
		X_v	46.129		
		S_x	0.113		
		S_w	0.0765		
		S_s	0.10		
		σ	4.14		
		0.3σ	1.242		
		0.10	<	1.242	

11.3. Stability

Three bottles of proficiency testing material for trace metals analysis in drinking water were analysed in duplicates in different days, ten bottles of anions were analysed in triplicate in different days in order to asses stability of samples for the period of duration of PT scheme. Metal analysis was carried out by ETAAS (Pb, Cd, Ni, Cr, Al, Cu and Mn); FIMS (Hg); FAAS (Fe and Zn) and FIAS (As). Analysis of anions was carried out by ion chromatography (IC). For the stability check the results were evaluated using bellow equation according to ISO 13528, where we compare the general average of the results obtained in the homogeneity check with the general average of the results obtained in the stability check. The results obtained from the stability check showed that the samples were adequately stable.

$$|\bar{y}_{,v} - \bar{x}_v| \leq 0.3\sigma$$

Where:

$\bar{y}_{,v}$: general average of the results obtained in the stability check

$\bar{x}_v$: general average of the results obtained in the homogeneity test

σ: standard deviation for proficiency assessment

The results of stability study are shown in Table 16 – Table 22.

Table 16. Stability results for Pb, Cd and Cr total

Pb				Cd				Cr			
t	**v**		$y_{t,v}$	**t**	**v**		$y_{t,v}$	**t**	**v**		$y_{t,v}$
	1	2			1	2			1	2	
1	27.07	27.13	27.1	1	7.65	7.59	7.62	1	30.28	29.79	30.03
2	26.98	27.09	27.03	2	7.51	7.39	7.45	2	29.78	30.27	30.02
3	26.94	26.95	26.94	3	7.48	7.46	7.47	3	29.94	30.11	30.02
	$y_{,v}$	27.01			$y_{,v}$	7.55			$y_{,v}$	30.19	
	$\| y_{,v} - x_{,v} \|$	0.01			$\| y_{,v} - x_{,v} \|$	0.1			$\| y_{,v} - x_{,v} \|$	0.175	
	σ	2.03			σ	0.7			σ	3.02	
	$0.3\ \sigma$	0.61			$0.3\ \sigma$	0.21			$0.3\ \sigma$	0.906	
	0.01	$<$	0.61		0.1	$<$	0.21		0.175	$<$	0.906

Table 17. Stability results for As, Hg and Ni

As				Hg				Ni			
t	**v**		$y_{t,v}$	**t**	**v**		$y_{t,v}$	**t**	**v**		$y_{t,v}$
	1	2							1	2	
1	28.87	28.69	28.78	1	3.54	3.48	3.51	1	29.48	29.55	29.51
2	28.57	28.63	28.6	2	3.49	3.5	3.49	2	29.62	29.7	29.66
3	28.9	28.75	28.82	3	3.38	3.55	3.46	3	29.55	29.8	29.67
	$y_{,v}$	28.81			$y_{,v}$	3.54			$y_{,v}$	29.64	
	$\| y_{,v} - x_{,v} \|$	0.01			$\| y_{,v} - x_{,v} \|$	0.025			$\| y_{,v} - x_{,v} \|$	0.05	
	σ	2.93			σ	0.51			σ	3.08	
	$0.3\ \sigma$	0.879			$0.3\ \sigma$	0.153			$0.3\ \sigma$	0.924	
	0.01	$<$	0.879		0.025	$<$	0.153		0.05	$<$	0.924

Table 18. Stability results for Cu, Fe and Mn

Cu				Fe				Mn			
t	**v**		$\mathbf{y_{t,v}}$	**t**	**v**		$\mathbf{y_{t,v}}$	**t**	**v**		$\mathbf{y_{t,v}}$
	1	2			1	2			1	2	
1	29.67	29.61	29.64	1	180.1	179.7	179.9	1	30.54	30.48	30.51
2	29.55	29.47	29.51	2	180.6	180.1	180.3	2	30.66	30.57	30.61
3	29.6	29.38	29.49	3	180.9	180.1	180.5	3	30.21	30.42	30.31
	$y_{,v}$	29.54			$y_{,v}$	180.1			$y_{,v}$	30.48	
	$\lvert y_{,v} - x_{,v} \rvert$	0.025			$\lvert y_{,v} - x_{,v} \rvert$	0.535			$\lvert y_{,v} - x_{,v} \rvert$	0.055	
	σ	2.27			σ	21.6			σ	2.28	
	0.3 σ	0.681			0.3 σ	6.48			0.3 σ	0.684	
	0.025	<	0.681		0.535	<	6.48		0.055	<	0.684

Table 19. Stability results for Al and Zn

Al				Zn			
t	**v**		$\mathbf{y_{t,v}}$	**t**	**v**		$\mathbf{y_{t,v}}$
	1	2			1	2	
1	155.8	155.4	155.6	1	360.6	361	360.8
2	155.3	154.8	155.1	2	359.8	360.4	360.1
3	154.9	155.7	155.3	3	360	360.3	360.2
	$y_{,v}$	155.7			$y_{,v}$	360.5	
	$\lvert y_{,v} - x_{,v} \rvert$	0.3			$\lvert y_{,v} - x_{,v} \rvert$	0.36	
	σ	15.4			σ	35.9	
	0.3 σ	4.62			0.3 σ	10.8	
	0.3	<	4.62		0.36	<	10.8

Table 20. Stability results for F^- and $PO4^{-3}$

F^-					PO_4^{-3}				
t	**v**			$y_{t,v}$	**t**	**v**			$y_{t,v}$
	1	2	3			1	2	3	
1	0.892	0.905	0.884	0.894	1	9.25	8.09	9.10	8.81
2	0.91	0.915	0.890	0.905	2	9.45	9.18	9.34	9.32
3	0.905	0.893	0.91	0.903	3	9.43	9.30	9.25	9.33
4	0.915	0.876	0.915	0.902	4	9.34	9.30	9.18	9.27
5	0.925	0.885	0.905	0.905	5	9.20	9.10	8.80	9.03
6	0.908	0.890	0.898	0.899	6	9.15	8.95	8.90	9.00
7	0.898	0.898	0.905	0.900	7	9.45	9.30	9.10	9.28
8	0.878	0.920	0.890	0.896	8	9.34	9.20	9.15	9.23
9	0.867	0.875	0.910	0.884	9	9.25	9.21	9.1	9.19
10	0.910	0.880	0.895	0.895	10	9.21	9.15	9.09	9.15
		$y_{,v}$	0.898				$y_{,v}$	9.162	
		$\|y_{,v}-x_{,v}\|$	0.014				$\|y_{,v}-x_{,v}\|$	0.208	
		σ	0.148				σ	1.06	
		0.3σ	0.044				0.3σ	0.318	
		0.014	<	0.044			0.208	<	0.318

Table 21. Stability results for Cl^- and NO_3^-

Cl^-					NO_3^-				
t		**v**		$y_{t,v}$	**t**	**v**			$y_{t,v}$
	1	2	3			1	2	3	
1	27.12	26.79	27.04	26.98	1	26.10	25.89	25.60	25.86
2	27.34	27.07	26.99	27.13	2	25.90	25.78	25.67	25.78
3	27.05	26.90	26.80	26.92	3	25.64	25.72	25.60	25.65
4	27.20	27.15	27.05	27.13	4	25.78	25.60	25.55	25.64
5	27.43	27.34	27.20	27.32	5	26.05	25.90	25.96	25.97
6	27.18	27.10	27.05	27.11	6	25.98	25.95	26.00	25.98
7	26.98	27.00	26.99	26.99	7	25.34	25.20	25.05	25.20
8	27.08	26.98	26.80	26.95	8	25.67	25.50	25.40	25.52
9	26.70	26.78	26.70	26.73	9	25.80	25.70	25.60	25.70
10	27.30	26.90	26.85	27.02	10	25.78	25.40	25.34	25.51
		$y_{,v}$	27.029				$y_{,v}$	26.682	
		$\|y_{,v}-x_{,v}\|$	0.072				$\|y_{,v}-x_{,v}\|$	0.1	
		σ	2.64				σ	2.49	
		0.3σ	0.792				0.3σ	0.75	
		0.072	<	0.792			0.1	<	0.75

Table 22. Stability results for NO_2^- and SO_4^{-2}

NO_2^-					SO_4^{-2}				
t	**v**			$y_{t,v}$	**t**	**v**			$y_{t,v}$
	1	2	3			1	2	3	
1	0.980	0.970	0.960	0.970	1	46.32	46.05	46.10	46.16
2	1.010	0.985	0.955	0.983	2	46.20	45.99	46.18	46.12
3	0.978	0.950	0.945	0.958	3	46.44	46.20	46.10	46.25
4	0.954	0.930	0.935	0.940	4	46.18	46.10	46.08	46.12
5	0.990	0.960	0.962	0.971	5	46.05	46.00	45.90	45.98
6	0.993	0.945	0.940	0.959	6	45.89	45.70	45.67	45.75
7	0.956	0.950	0.940	0.949	7	45.98	45.89	45.80	45.89
8	0.980	0.970	0.960	0.970	8	46.12	45.99	45.89	46.00
9	1.050	0.995	0.998	1.014	9	46.13	46.00	45.98	46.04
10	0.980	0.960	0.970	0.970	10	46.08	45.80	46.20	46.03
		$y_{,v}$	0.968				$y_{,v}$	46.034	
		$\lvert y_{,v}-x_{,v}\rvert$	0.008				$\lvert y_{,v}-x_{,v}\rvert$	0.095	
		σ	0.15				σ	4.14	
		0.3σ	0.047				0.3σ	1.242	
		0.008	<	0.047			0.095	<	1.242

APPENDIX C

Table 23. Results for trace metals concentration in drinking water from accredited laboratories (μg/l)

Lab.	Pb		Cd		Cu		Zn		Fe		Mn		Cr		As		Al		Ni		Hg	
	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S
1	31.25	0.092	7.91	0.05	28.94	0.11	380.23	0.25	194.2	0.56	38.11	0.08	32.54	0.02	25.65	0.18	189.6	0.11	35.2	0.26	3.68	0.01
2	29.55	0.21	8.12	0.04	31	0.58	379.67	2.20	193.32	0.78	38.21	0.15	32.42	0.11	26.12	0.56	189.2	0.89	33.2	0.60	3.64	0.11
3	32.45	1.03	8.15	0.87	29. 4	1.23	378.7	1.19	192.78	0.80	38.08	0.54	33.12	0.32	25.1	1.18	187.4	0.78	34.9	0.82	3.70	0.05
4	31.9	0.56	7.98	0.56	29.9	0.98	371.6	1.89	192.9	0.23	37.78	0.22	30.98	0.15	25.39	0.78	185.9	1.55	34.2	1.02	3.60	0.02
5	32.6	0.15	8.31	0.43	31.6	0.68	376.7	1.45	194.1	1.34	37.92	0.55	32.76	0.89	25.18	0.55	183.2	2.34	33.6	0.98	3.57	0.21
IPH	27.1	0.24	7.59	0.65	29.52	1.12	360.6	2.11	180.9	1.89	30.53	1.05	30.17	0.78	28.6	0.80	155.7	0.90	29.8	1.15	3.54	0.08

Table 24. Results for anion concentration in drinking water from accredited laboratories

Laboratory	F^- (mg/l)		PO_4^{-3} (mg/l)		Cl^- (mg/l)		NO_3^- (mg/l)		NO_2^- (mg/l)		SO_4^{-2} (mg/l)	
	X	S	X	S	X	S	X	S	X	S	X	S
1	0.934	0.012	8.68	0.112	24.7	0.21	23.76	0.32	1.01	0.044	43.13	0.71
2	0.955	0.0232	8.72	0.15	25.12	0.12	23.40	0.25	1.13	0.032	44.20	0.66
3	0.937	0.0147	8.58	0.22	25.43	0.16	24.45	0.28	1.12	0.022	43.01	0.43
4	0.970	0.018	8.88	0.18	24.62	0.13	23.56	0.44	1.08	0.038	44.00	0.54
5	0.942	0.025	8.76	0.10	25.3	0.15	23.85	0.22	1.18	0.027	42.14	0.27
IPH	0.912	0.014	9.37	0.12	26.62	0.17	25.58	0.48	0.972	0.049	46.13	0.82