ORIGINAL ARTICLE

J. Chem. Metrol. X:X (201X) X-X

journal of chemical metrology

Proficiency testing for determination of pH and electrolytic conductivity in water and soil samples

Emrah Uysal[1*], Lokman Liv[1] and Fatma Akçadağ[2]

[1]Electrochemistry Laboratory, TUBITAK UME (National Metrology Institute), Gebze, Türkiye
[2]Reference Materials Laboratory, TUBITAK UME (National Metrology Institute), Gebze, Türkiye

(Received October 09, 2019; Revised December 07, 2019; Accepted December 10, 2019)

Abstract: According to ISO 17025:2017, the testing laboratories are required to confirm the measurement accuracy with proficiency testings or international comparisons. For this purpose, the proficiency testings for pH and conductivity measurements in water and soil are organized by TUBITAK UME twice a year. In this study, the preparation and analysis of the samples according to BS EN ISO 10523:2012, ISO 7888:1985, ISO 10390:2005 and ISO 11265:1996 and the evaluation of the results according to ISO 17043:2010 were carried out. pH and electrolytic conductivity (EC) values were determined by a pH meter and a conductivity meter for this study. Based on the results of the participants, they have a chance to improve the accuracy and reliability of their measurement results as observing the performances of other laboratories.

Keywords: Electrolytic conductivity; pH; drinking water; soil; proficiency testing.

1. Introduction

pH and electrolytic conductivity (EC) measurements have an indispensable role in many diverse areas. Researchers and technicians in scientific and industrial laboratories use these measurements for quality control and human health. Therefore there is a great demand to ensure quality for these important measurements that are used in so many branches and also they must comply with the standards and technical requirements [1]. pH and EC play a critical role throughout industrial processes like food industry. For example, in some situations of this kind of processes, careful monitoring and controlling of temperature are required to slow down bacteria activity to prevent over acidification. Optimal control is obtained by pH measurements. However, accurate and traceable pH measurement needs to be realised to take concrete steps for assuring reliable product quality [2]. The prior condition for the international acceptance is reliable measurements. Measurement means to compare. Hence, comparability is required recognised references to which the standard reference materials used for calibration and verification of pH meter and conductivity meter devices can be traced [3]. pH is a measure of the hydronium ion activity and EC is a measure of the transmission of

---

[*] Corresponding author E-Mail: emrah.uysal@tubitak.gov.tr

The article was published by ACG Publications
http://www.acgpubs.org/journal/journal-of-chemical-metrology © July-December 2019 EISSN:1307-6183
DOI: http://doi.org/10.25135/jcm.31.19.11.1439

electric current. Both show the quality of water and soil these are parameters used for process control and quality control in a wide range of industrial studies. Some of these industries must perform accurate and traceable measurements in order to comply with the limits set by the authorities for selling and exporting their products [4]. Both private and government laboratories ought to be accredited in order to comply with the ISO/IEC 17025:2017 standard. Hereby the laboratories will gain a strong quality control and assurance system. Proficiency Testing (PT) is a significant tool for reveal and evidence the measurement results of the laboratories. PT is also an external quality control tool which give a chance to individual laboratories for comparing their performance with other laboratories [5-9]. The main objective of this requirement is to provide objective evidence of capability of laboratories which are in accreditation process to produce data for the accreditation body. After the proof is approved, this will also give advantage to the laboratories for their clients and potential customers. However, participation in proficiency testing studies also provide a significant feedback in the internal monitoring of a laboratory's quality system [10].

In order to increase awareness of accurate pH and EC measurements in Turkey and also maintaining the quality of these measurements, Chemistry Group Laboratories of TUBITAK UME have been organizing PT schemes for pH and EC measurements since 2005. Participant laboratories determine pH and EC values in water samples provided by TUBITAK UME. Based on the results of the participants, they can improve the accuracy and reliability of their measurement results as observing the performances of other laboratories. Because the participating laboratories have a chance to compare their measurement results with results of the other laboratories.

2. Experimental

2.1. Reagents and Solutions

Disodium hydrogen orthophosphate (Na_2HPO_4), potassium dihydrogen orthophosphate (KH_2PO_4) and potassium chloride (KCl) were obtained from Merck, Emsure level.

UME CRM 1401, 1402 and 1403 (pH 4, 7 and 10) certified reference materials (CRMs) for pH measurements were used for calibration of pH meter and Hanna HI7031L/C (1413 µS/cm) solution traceable to NIST was used for calibration of conductivity meter.

2.2. Apparatus

Milli-Q Integral 10 water purification system was used to produce ultrapure water (18.2 MΩ) for preparation of all solutions.

New Brunswick Scientific Innova 2100 Platform Shaker was used to homogenize the water samples and to shake the soil suspensions.

Turbula T10B three-dimensional mixer was used to homogenize the soil samples.

Mettler Toledo Seven Easy pH meter was used for pH and Mettler Toledo Seven Excellence Multiparameter conductivity meter was used for EC measurements.

HDPE containers and bottles were used for the storage and bottling the proficiency testing solutions, respectively.

2.3. Sample Preparation and Analysis Procedure for Water Samples

For preparation of pH in water samples, Na_2HPO_4 and KH_2PO_4 were used in the amounts declared in IUPAC pH standard for 10 kg ultrapure water in a 10 L HDPE container [11]. For preparation of EC in water samples, proper amount of KCl corresponding to about 1500 µS/cm was weighted and then added into a 10 L HDPE container in which 10 L deionized water was filled. In order to obtain homogenous mixtures, both samples were mixed for 4 hours by the platform shaker with a 110 rpm speed. After the homogenization process, the samples were transferred into 250 mL HDPE bottles and labelled according to the appropriate format defined in the TUBITAK UME Quality System. 10 samples were randomly selected for homogeneity test and 3 samples were randomly selected for stability test for each proficiency test. Homogeneity measurements were made immediately after the samples were prepared. Stability was tested one month after the PT samples were prepared.

pH and EC measurements were performed according to BS EN ISO 10523:2012 and ISO 7888:1985, respectively [12-13].

Offset voltage and slope of the combined pH electrode were checked after the calibration step using pH 4, 7 and 10 CRMs. The acceptable offset voltage is between ± 15 mV and the acceptable slope is between (95-102)%. pH measurements were performed at 20 °C. Cell constant of the conductivity probe was determined by 1413 μS/cm standard solution and the acceptable deviation is between ± 2%. EC measurements were performed at 25 °C. Each sample was measured twice for both PTs. The evaluation of the results according to ISO 17043:2010 were carried out [7].

2.4. Sample Preparation and Analysis Procedure for Soil Samples

The soil sample was bottled and labelled according to the appropriate format defined in the TUBITAK UME Quality System after 4 hours of homogenization with three-dimensional mixer after grinding and sieving to reduce the size of the sample to 500 microns or less. Homogeneity and stability sample selections were made as the same as water samples.

pH and EC measurements were performed according to ISO 10390:2005 and ISO 11265:1996, respectively [14-15].

The acceptance criteria for calibration process and temperature for measurements were the same as in water samples. 7 g of soil sample was weighed into a 50 mL falcon tube and then 35 mL of 1 mol/L KCl was added for pH measurement or 35 mL of ultrapure water was added for EC measurement. The suspended samples should be shaken at 180 rpm for 60 minutes for pH measurement and for 30 minutes for EC measurement. After shaking, the samples were allowed to rest for 20 minutes and the supernatant of each sample was measured twice for both PTs. The evaluation of the results according to ISO 17043:2010 were carried out [7].

2.5. The Procedure of Proficiency Testing Scheme

A protocol and a program were developed by the coordinator and technical experts for the analysis. The protocol includes some information about sample preparation, distribution, storage and necessary parameters for determination of the parameters. The protocols of proficiency testing are always published on the TUBITAK UME's website. Another important point is that, the identities and the results of the participating laboratories are reported confidentially as each laboratory is assigned with a different participant number [16].

The evaluation of the homogeneity and stability test results were evaluated according to ISO 13528:2015 [17].

The participant laboratories were free to choose a method for pH and electrolytic conductivity measurements in water and soil samples although it was recommended for them to use the same method and operator for their routine analysis. However, the measurement temperatures for pH and EC should be 20 °C and 25 °C, respectively. After measurements have been done, the laboratories reported their results using an online software developed by TUBITAK UME.

Z-scores for each laboratory were determined statistically according to ISO 17043:2010 to evaluate the results of participant laboratories [18-21]. The reports were prepared by the technical group of TUBITAK UME and then published on the TUBITAK UME's website. The attendance certificates were sent to the participants at the end of this period.

In order to ensure confidentiality, each participant in the scheme was defined with a different laboratory number. The numbers were used for reporting the results without unveil the identities of participant laboratories. All information provided by the participants of the proficiency testing were treated as confidential.

2.6. Estimation of Measurement Uncertainty

Measurement uncertainties for the determination of assigned values during the proficiency testing study were estimated in accordance with GUM “Guide to the Expression of Uncertainty in Measurement” after the measurements that were performed in TUBITAK UME Electrochemistry Laboratory [22]. The expanded uncertainty of the assigned value was stated as the standard uncertainty of measurement multiplied by the coverage factor k=2, which for a normal distribution corresponds to a coverage probability of approximately 95%.

3. Results and Discussion

3.1. Homogeneity and Stability Studies

Homogeneity results of the PT samples are given in Table 1.

Table 1. Homogeneity measurement results

	pH				**EC (µS/cm)**			
	Water		**Soil**		**Water**		**Soil**	
	1	2	1	2	1	2	1	2
Measurement results	6.91	6.90	7.64	7.65	1551	1579	2300	2300
	6.90	6.91	7.65	7.64	1551	1552	2300	2332
	6.91	6.91	7.64	7.64	1550	1551	2332	2332
	6.91	6.91	7.65	7.64	1551	1552	2344	2344
	6.90	6.90	7.64	7.65	1551	1554	2345	2302
	6.91	6.90	7.65	7.65	1554	1548	2302	2302
	6.90	6.90	7.65	7.64	1550	1547	2290	2288
	6.90	6.90	7.64	7.64	1549	1549	2279	2314
	6.91	6.91	7.64	7.64	1550	1550	2317	2315
	6.90	6.90	7.65	7.65	1555	1553	2324	2319

Evaluation of homogeneity according to ISO 13528:2015 includes the calculation of the between-samples standard deviation (s_s) and the standard deviation for proficiency assessment (σ). If the Eq. 1 is valid, then PT samples are considered to be prepared homogeneously.

$$s_s \leq 0.3\sigma \tag{1}$$

Three bottles for testing stability of the PT samples were stored at the laboratory conditions which are (21 ± 3) °C and two parallel measurements were performed for each sample. Stability results of the PT samples are given in Table 2.

Table 2. Stability measurement results

	pH				EC (µS/cm)			
	Water		**Soil**		**Water**		**Soil**	
	1	2	1	2	1	2	1	2
Measurement results	6.91	6.91	7.65	7.59	1527	1526	2314	2314
	6.91	6.91	7.65	7.62	1526	1526	2303	2304
	6.91	6.91	7.64	7.63	1522	1527	2309	2307

Evaluation of stability according to ISO 13528:2015 includes the comparison of the average values from the homogeneity test ($\bar{x}_{.v}$) and the stability test ($\bar{y}_{.v}$)with σ by using Eq. 2. If the Eq. 2 is valid, then PT samples are considered to be stable in the PT period. Homogeneity and stability test results are shown in Table 3.

$$|\bar{x}_{.v} - \bar{y}_{.v}| \leq 0.3\sigma \tag{2}$$

Table 3. Homogeneity and stability test results

	pH		EC µS/cm	
	Water	**Soil**	**Water**	**Soil**
s_s	0.003	0.001	1.3	13.9
$\lvert\bar{x}_{.v}-\bar{y}_{.v}\rvert$	0.005	0.014	26.7	5.7
0.3σ	0.051	0.270	34.5	34.6

It was said that the both water and soil samples for pH and EC were homogeneous and stable because 0.3σ was higher than s_S and $\lvert\bar{x}_{.v}-\bar{y}_{.v}\rvert$.

3.2. Evaluation of the Participant Laboratory Results

There is no any certain rule to assign a reference value in PT. The preparation, determination of assigned value and standard deviation of the PT samples were done by the TUBITAK UME researchers. If TUBITAK UME results are significantly different from the results of the participants, the median is accepted as the assigned value. In this study, the assigned values were calculated from the homogeneity and stability results performed by TUBITAK UME. Z-scores for each laboratory were determined statistically according to ISO 17043:2010 to evaluate the results of participant laboratories [7]. These were calculated by using the assigned values and standard deviation. However, different methods can be used to compare the results of the analysis. The z-score is calculated using Eq. 3:

$$z_i = \frac{x_i - \bar{x}}{\sigma} \tag{3}$$

where x_i is the result of i participant, $\bar{x}$ is the assigned value and σ is the standard deviation of the assigned value. As is well known, the results are satisfactory if $z \leq |2.0|$; it is questionable if z is between 2.0 and 3.0 and it is unsatisfactory if $z \geq |3.0|$.

Some analytical and statistical parameters and distribution of z-scores are given in Table 4 and Table 5, respectively.

Moreover, the distribution of the participant laboratory results are shown in Figure 1- Figure 4. Green lines in the figures defines the z-scores between ±2 and red lines defines the z-scores between ±3.

Table 4. Some analytical and statistical parameters for PT schemes

	pH		**EC µS/cm**	
	Water	**Soil**	**Water**	**Soil**
Number of results	32	12	26	7
Assigned value	6.87	7.70	1533	2300
Mean	6.89	7.67	1516	2304
Median	6.87	7.70	1539	2307
Standard deviation	0.17	0.58	115	173
Minimum value	6.44	6.47	1335	2120
Maximum value	7.16	8.32	1615	2430

Table 5. Distribution of z-scores

		|z| ≤ 2		**2 < |z| < 3**		**|z| ≥ 3**		**Total number of scores**
		Number of scores	**%**	**Number of scores**	**%**	**Number of scores**	**%**	
pH	**Water**	31	96.8	1	3.2	0	0	32
	Soil	11	91.7	1	8.3	0	0	12
EC	**Water**	26	100	0	0	0	0	26
	Soil	7	100	0	0	0	0	7

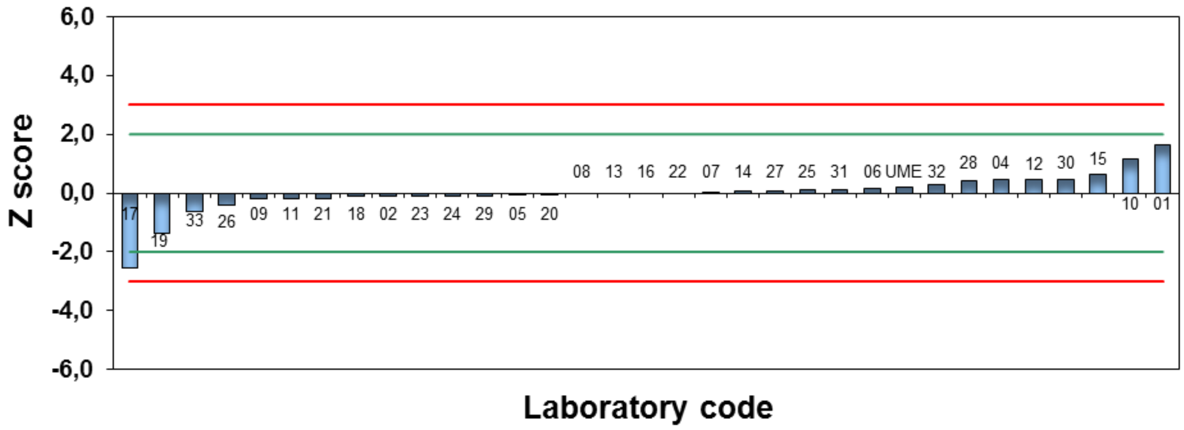

Figure 1. Distribution of pH results in drinking water samples

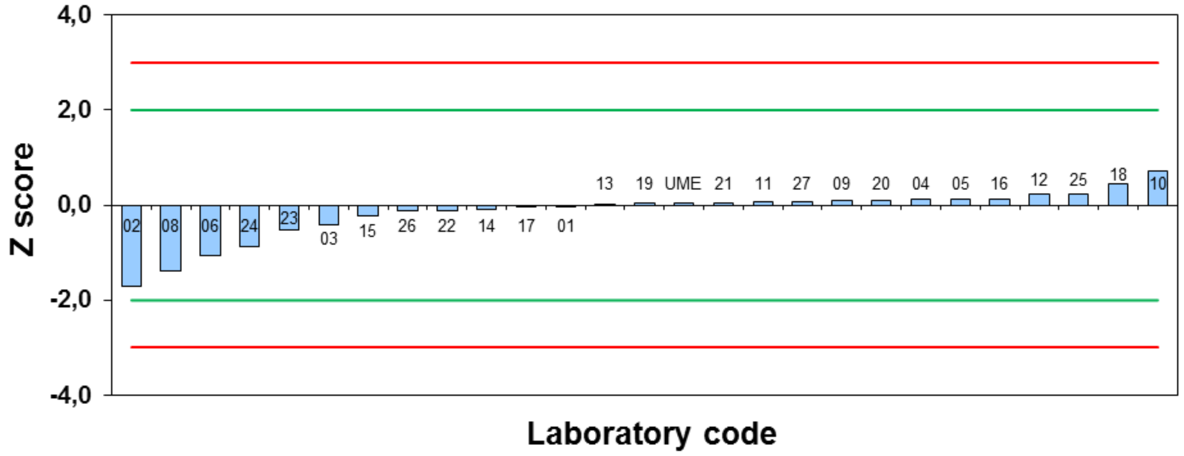

Figure 2. Distribution of EC results in drinking water samples

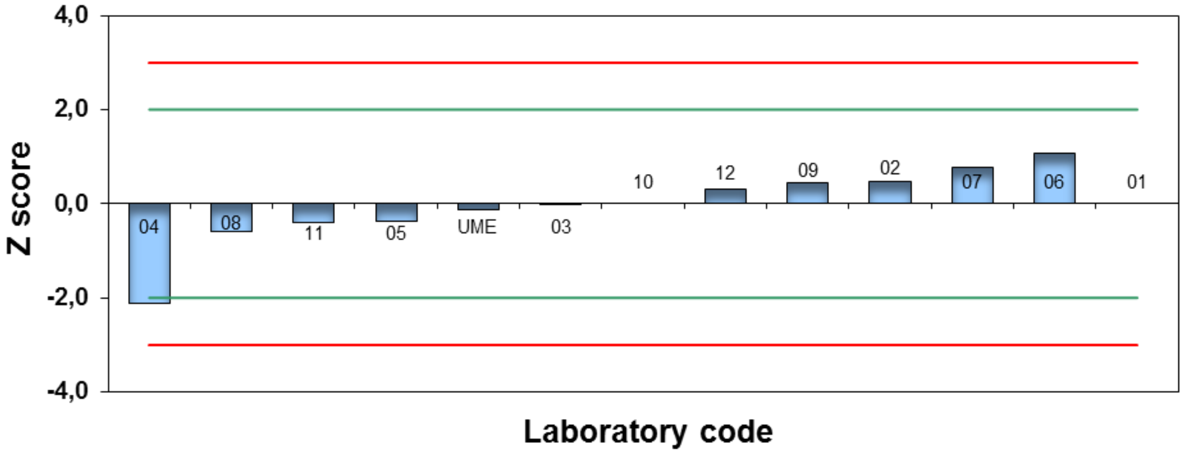

Figure 3. Distribution of pH results in soil samples

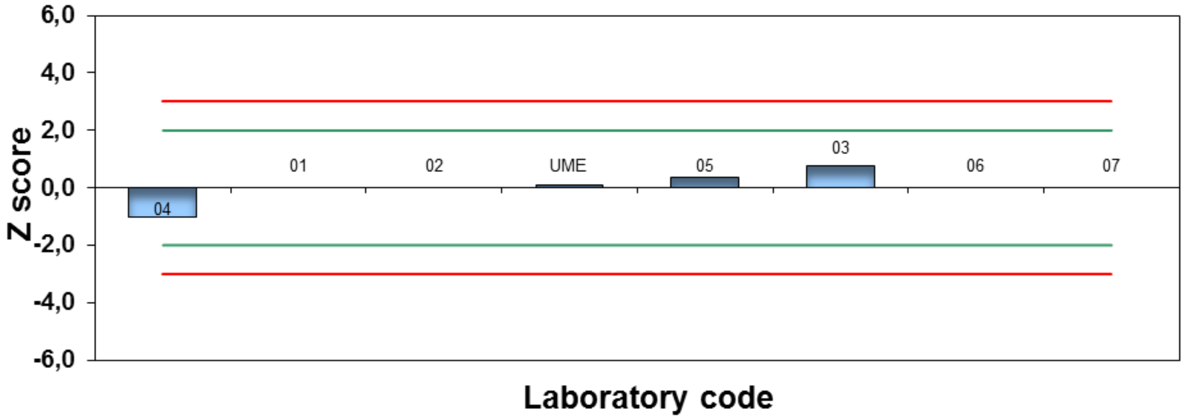

Figure 4. Distribution of EC results in soil samples

The histogram plot for all PTs using z-scores was drawn as is given in Figure 5. It was found that 97.5% of the results were in the reliable range as |z| ≤ 2.

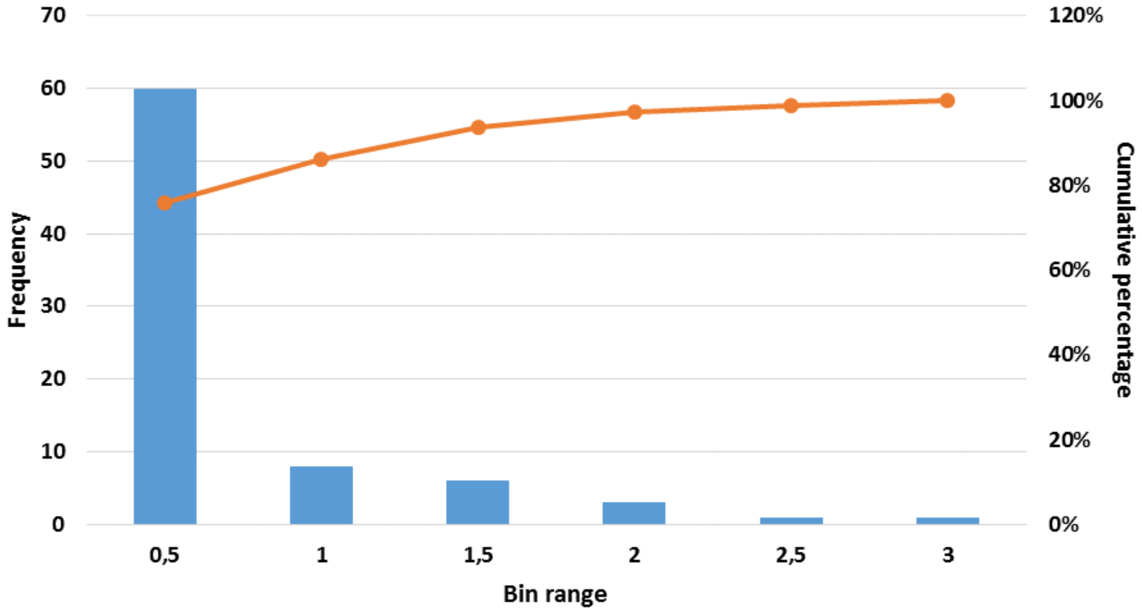

Figure 5. Histogram plot for PTs using z scores

3.3. Evaluation of the Measurement Uncertainty

During the determination of the reference values which were based on the measurements performed at TUBITAK UME, the components of the uncertainties for pH measurements in water and soil samples are standard uncertainties derived from the standard buffer, calibration deviation, temperature and repeatability uncertainties. The components of the uncertainties for electrolytic conductivity measurements in water and soil samples are standard uncertainties derived from the reference solution, instrument resolution, temperature and repeatability.

The uncertainty budget of pH measurement in water and soil samples are shown in Table 6.

Table 6. The uncertainty budget for pH measurements

	Water	**Soil**
Standard buffer uncertainty	0.01	0.01
Calibration deviation uncertainty	0.029	0.029
Temperature	0.002	0.002
Repeatability	0.001	0.001
Standard combined uncertainty	0.03	0.03
Expanded uncertainty (k = 2)	0.06	0.06

The uncertainty budget of electrolytic conductivity (EC) measurements in water and soil samples are shown in Table 7.

Table 7. The uncertainty budget of EC measurements

	Water (µS/cm)	**Soil (µS/cm)**
Reference solution uncertainty	0.025	0.025
Resolution	0.0033	0.0033
Temperature	0.0005	0.0005
Repeatability	1,470	4,380
Standard combined uncertainty	1.47	4.38
Expanded uncertainty (k = 2)	2.94	8.76

4. Conclusions

Proficiency testing for determination of pH and electrolytic conductivity in water and soil samples were organized, performed and evaluated according to the ISO standards. The results of homogeneity, stability and distribution of z-scores show that these proficiency tests were successfully performed. When the expanded uncertainty values in the uncertainty budget for the measurement results given in Table 6 and Table 7 are compared with the values in the relevant international standards, it is worth emphasizing that this proficiency test conducted between the limits of the uncertainty values of the standards.

In addition, when the total number of laboratories for 4 tests was examined, only 2 laboratories from 77 laboratories had a z score between 2 and 3. This situation is also seen clearly from the drawn histogram plot. Both show that the satisfactorily results were obtained. Moreover, the proficiency testing gives a chance to the participant laboratories to find out their problems in particular issues. The organizers hope that the study will help them to choose the right direction for their future studies.

ORCID

Emrah Uysal: 0000-0001-5783-1874
Lokman Liv: 0000-0001-8008-1012
Fatma Akçadağ: 0000-0003-4000-3874

References

[1] World Health Organization (WHO). (1996). Trace elements in human nutrition and health, *WHO*, Switzerland.

[2] Queeney, K (2007). The importance of pH measurement in assuring product quality. https://www.manufacturing.net/article/2007/06/importance-pH-measurement-assuring-product-quality Accessed 13.05.2019

[3] P. Spitzer, and B. Werner, (2002). Improved realibility of pH measurements, *Anal. Bioanal. Chem*, **374**, 787-795.

[4] H. D. Jensen (2000). Towards and improved primary standard for electrolytic conductivity. *DFM*, Denmark.

[5] P. Bedson, T.J. Farrant, S. L. R. Ellison, and V. J. Barwick (2009). Practical statistics for the analytical scientist: A bench guide, *Royal Society Chemistry*, Cambridge, United Kingdom.

[6] International Organization for Standardization (ISO). (2005). ISO 13528:2005 Statistical methods for use in proficiency testing by interlaboratory comparisons, *ISO*, Switzerland.

[7] International Organization for Standardization (ISO). (2010). ISO/IEC 17043:2010 Conformity assessment - General requirements for proficiency testing, *ISO*, Switzerland.

[8] International Organization for Standardization (ISO). (2005). ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories, *ISO*, Switzerland.

[9] R. E. Lawn, M.Thompson and F.R. Walker (1997). Proficiency testing in analytical chemistry, *Royal Society Chemistry*, Cambridge, United Kingdom.

[10] T. Näykki, L. Jalukse, I. Helm, and I. Leito (2013). Dissolved oxygen concentration interlaboratory comparison: What can we learn? *Water*, **5**, 420-442.

[11] R. P. Buck, S. Rondinini, A.K. Covington, F.G.K. Baucke, C.M.A. Brett, M.F. Camões, M.J.T. Milton, T. Mussini, R. Naumann, K.W. Pratt, P. Spitzer, and G.S. Wilson (2002). Measurement of pH. Definition, standards, and procedures, *Pure Appl. Chem.*, **74**, 2169-2200.

[12] British Standards Institution (BSI). (2012). BS EN ISO 10523:2012 Water quality - Determination of pH, *ISO*, Switzerland.

[13] International Organization for Standardization (ISO). (1985). ISO 7888:1985 Water quality - Determination of electrical conductivity, *ISO*, Switzerland.

[14] International Organization for Standardization (ISO). (2005). ISO 10390:2005 Soil quality - Determination of pH, *ISO*, Switzerland.

[15] International Organization for Standardization (ISO). (1996). ISO 11265:1996 Soil quality - Determination of the specific electrical conductivity, *ISO*, Switzerland.

[16] E. Uysal, F. Akçadağ, and N. Tokman (2014). Proficiency testing for determination of metals in tomato paste, *J. Chem. Metrol*., **8**, 13-26.

[17] International Organization for Standardization (ISO). (2015). ISO 13528:2005 Statistical methods for use in proficiency testing by interlaboratory comparison, *ISO*, Switzerland.

[18] S.L.R. Ellison, and A. Williams (2012). EURACHEM/CITAC Guide quantifying uncertainty in analytical Measurement, *EURACHEM/CITAC*, United Kingdom.

[19] B.N. Taylor and C.E. Kuyatt (1994). Guidelines for evaluating and expressing the uncertainty of NIST measurement results, *NIST*, Washington, USA.

[20] JCGM (2012). International vocabulary of metrology - Basic and general concepts and associated terms (VIM), Third Edition, *JCGM*, France.

[21] International Organization for Standardization (ISO). (2002). ISO 5725-2:1994/COR 1:2002 Accuracy (trueness and precision) of measurement methods and results, *ISO*, Switzerland.