Eurasian Journal of Environmental Research
EJERE, Vol. 4, Issue 1, pp. 1-9, June 2020

ISSN 2602-2990, TURKEY
Research Article

A INTER-LABORATORY COMPARISON TEST FOR ELECTROCHEMICAL ANALYTICAL METHODS IN REAL WASTEWATER SAMPLE: Z-SCORE MODEL AND PARTICIPANTS EFFECT

Hulusi Demircioğlu[1*], İlgi Karapınar[2]

[1] Dokuz Eylul University, Institute of Marine Sciences and Technology, Izmir, Turkey
e-mail: h.demircioglu@deu.edu.tr

[2] Dokuz Eylul University, Department of Environmental Engineering, Tinaztepe Campus, Izmir, Turkey

* Corresponding Author: Hulusi Demircioğlu

Received: 31/01/2020 **Accepted:** 01/05/2020

ABSTRACT

The study was conducted to evaluate the z-scores of accredited and non-accredited laboratories for the electrochemical analysis namely pH, conductivity and salinity through an inter-laboratory comparison test carried out on real wastewater samples. The participants were small scale 16 non-accredited and 9 accredited wastewater analysis laboratories in Turkey. The samples from a wastewater treatment plant were first collected from influent and effluent lines. The third sample was prepared by mixing the influent and effluent water samples to obtain three different levels of analysis as high, low and medium, respectively. pH, conductivity or salinity are the measurements based on electrochemical analytical methods in which the influence of the other factors such as technical staff ability on the measurement is limited. However, the method used in z-score calculation could have a substantial effect on the z-score performance of a laboratory. Therefore, three different z-score calculation approaches using standard deviation (SD) for proficiency assessment and different assigned values were applied to the inter-laboratory comparison test results. The assigned value was determined through average, and median of individual groups named as accredited or non-accredited laboratories. The results indicated that the method used in z-score calculation does not substantially affect the scores of the laboratory. No population quality effect on the z-score exists. The laboratory with low performance will not pass the comparison test whatever the z-score calculation method.

Keywords: *Inter-laboratory comparison test, Conductivity, pH, Salinity, Wastewater, z-score.*

1. INTRODUCTION

The environmental analysis quality is getting more and more significant in Turkey. There are more than 200 environmental testing laboratories in the country. They are serving to the sector for the analysis of water, wastewater, air emissions and noise. These laboratories are certificated by the Ministry of Environment and Urban Planning and then accredited by TÜRKAK. Certifications of these laboratories can be made as pre-certified or certified by the Ministry. None of the testing laboratory can do analysis without these certification and accreditation. The laboratories must satisfy all the quality assurances defined in ISO 17025.

One of the major parameters concerned in certification or accreditation process is inter-laboratory comparison test (ILC) or proficiency test (PT). Proficiency testing by interlaboratory comparisons is used to determine the performance of individual laboratories for specific tests or measurements, and to monitor the continuing performance of laboratories. In statistical language, the performance of laboratories can be described by three properties: laboratory bias, stability and repeatability. Proficiency testing by interlaboratory comparisons provides, in general, information about laboratory bias (TS EN ISO / IEC 17043, 2010).

The most critic statistical calculation steps of the proficiency testing are determination of the assigned value. Assigned values should be determined to evaluate participants fairly, yet to encourage agreement among test or measurement methods. The procedure used for assigned value determination is explained, in detail, in standard called statistical methods for use in proficiency testing by interlaboratory comparisons (TS ISO 13528, 2015). It is stated that this is accomplished through selection of common comparison groups and the use of common assigned values, wherever possible. In general, the assigned values need to be determined by expert judgment or from announced assigned value of the reference material (RM) used in PT. In some cases, a proficiency testing provider may use a consensus value, as defined by agreement of a predetermined majority percentage of responses (e.g. 80% or more). However, the percentage used should be determined based on objectives for the proficiency testing scheme and the level of competence and experience of the participants.

The results of these types of tests are indicator of quality in analysis of samples. They also, sometimes, considered as validation of the test method used or recently developed. It has been accepted that ILC or PT increases the measurement quality of the laboratories and, in addition, competence of the indoor laboratories with the international ones. Because, laboratories pay more attention to the traceability of reference standard materials, calibration of the equipment and education of the technical staff to increase their ILC or PT scores after a several failed score they got. However, the quality of ILC and PT schemes is another important parameter to be considered by the participants. High quality ILC and PT schemes should have large number of participants, high quality testing materials and a good reporting procedure. The low participation number, large variation in the participating laboratory qualities or the concentration of the testing material may positively or negatively affect the z-score performance of the laboratories. The z-score performance of a laboratory could depend on the analytical method used, the type of the analysis and the ability of the technicians. The z-score is combination of all these factors. Therefore, it must be well determined by using proper calculation methods in order to provide the correct information about the quality of the laboratory.

Although the Ministry and TURKAK substantially emphasize the importance of ILC/PT and pushes the laboratories to participate, the level of participation is not at desired level for the time being. One of the reasons for this situation is high costs of ILC and PT since the main providers of PT are companies from EU and USA. They provide very high quality testing materials, they are accredited and expecting a good deal of profit from these tests. The other one is no sufficient national PT providers. The only national PT provider in Turkey for environmental samples is TUBITAK UME to the best of our knowledge. They started providing PTs with limited number of parameters. But they progress on increasing the number of parameters for the PTs. The number of these types of organizations should be increased in Turkey and then they must be accredited for ISO 17043. In other words, there must be well trusted PT providers with wide range of testing schemes. Until the time to achieve this, the most available and suitable approach is to organize inter-laboratory comparison tests. ILC will make the laboratories get used to PTs, to find out the reasons for their low quality results and to have opportunity to improve their qualities to be able to compete with other international testing laboratories. However, there are certain limitations of ILC as it was discussed for PT. The number of participant is the major factor. But, the more important parameter is the statistical test used in comparison of the laboratories to determine that if one is succeeded or failed. Another one is the testing method used in comparison test. It substantially affects the performance of the laboratory. Therefore, a new statistical method is necessary for ICLs and may be for PTs based on analytical method, equipment etc.

The statistical methods used in calculation of the results have certain limitations. These methods should be compared with respect to sample type, analytical method or the type of the population. The deviations in the results with respect to the statistical methods should be stated. In other words the strong and weak points of the current statistical methods should be investigated. New evaluation methods should be developed as an alternative to the current statistical practices if necessary.

By considering all these facts about the z-score and need for PTs or ILC in Turkey, a simple ILC test was organized by DEU Environmental Engineering Department Testing Laboratory to show the limitations and advantages of ICL test. The main aim was to show the effect of z-score calculation methods on the quality determination of a laboratory.

2. ILC TEST ORGANIZATION BY DEU.

2.1. Participant and Organization:

The ILC was organized by DEÜ. DEU Department of Environmental Engineering Testing Laboratories has been accreditated since 2006. Eight years experience in management of existing quality and significant efforts to upgrade and improve the quality made the laboratory ready to organize ILCs. A simple ILC test was organized by DEU Environmental Engineering Department Testing Laboratory to show the limitations and advantages of ICL test in the concept of this paper. In inventory study was carried out to picture the potential for ILC test and PT tests in Turkey.

ILC participants were small-scale 16 non- accredited wastewater analysis laboratories and 9 accredited laboratories that give measurement service to the sector. All participants were volunteers to take a part in ILC.

2.2 Samples

The real wastewater samples were used in the test. Samples were collected from a domestic wastewater treatment plant in Izmir and then transferred to the participating laboratories located in the vicinity of Izmir. Three different samples were prepared; influent, effluent of the treatment plants and mixture of these two samples were used in order to obtain three different concentrations (levels) of parameters. Those concentrations correspond to low, high and medium concentrations.

In order to observe the consistency of the laboratories with their own results, EMV (Estimated Medium Value) was calculated. EMV is an average value obtained by considering 50% mixture of high concentration and low concentration.

Nearly 70 Liter sample were taken from influent and effluent point of wastewater treatment plant and distributed to the container. All sample containers were labeled with number, which did not include any information about the sample characteristics. Depending on the laboratory locations, four vehicles were organized for distributing the samples. All vehicles were equipped with coolers to ensure cold chain. All samples were delivered with test protocols in 3 hours to the laboratories for routine analysis.

There were no method limitations for the analysis of samples. Especially, laboratories were informed to complete tests under routine applications. Usually, accredited laboratories prefer International Standard Methods but non-accredited laboratories didn't give the method they used (Table 1). There the analytical method for the non-accredited ones were given as Not Reported (NR). But the brand name of the equipment was given for the corresponding analysis.

Table 1. ILC Test Methods used by Accredited Laboratories

Accredited Lab code	pH	Conductivity	Salinity
AC1	SM 4500 H^+ B	SM 2510 B	SM 2520 B
AC2	SM 4500 H^+	SM 2510 B	SM 2520 B
AC3	SM 4500 H^+ B	SM 2510 B	NR
AC4	SM 4500 H^+ B	NR	SM 2520 B
AC5	TS ISO 10523	TS 9748	TS 8108
AC6	TS ISO 10523	SM 2510 B	NR
AC7	SM 4500 H^+	SM 2510	NR
AC8	TS EN ISO 10523	NR	NR
AC9	SM 4500 H^+ B	TS 9748	NR

2.3. z-Score Calculation

The laboratory performances were evaluated by z-score. General z-score calculation equation is given below (TS SO 13528) ;

$$\boldsymbol{z} = \frac{(\boldsymbol{x}-\boldsymbol{X})}{\boldsymbol{\sigma_{PT}}} \qquad \text{(eq.1)}$$

where,
X: is the participant's result, X: is the assigned value.$\boldsymbol{\sigma}_{PT}$: is the standard deviation for proficiency assessment (SDPA)

In order to show the effect of z-score calculation method on the performance of the laboratories, different assign value and $\boldsymbol{\sigma}_{PT}$ were used as given in Table 2.

Table 2. Z-score calculation parameters.

Lab. Group	X (Assign value)	$\boldsymbol{\sigma}_{PT}$
Accredited Labs	Average, Median	MADe
Non accredited Labs	Average, Median	MADe
All Labs.	Average	MADe
All Labs.	Average	Std.Dev

4. RESULTS

4.1. pH Values and z-scores.

Table 3 depicts the results for pH of influent, effluent and mixture samples as well as the method used for the measurements by the non-accredited and accredited laboratories. The reported influent pH values with the averages of individual groups were also presented in Figure 1. As it can be seen from the figure, the reported values do not change substantially. It varies between 7.20- 7.80 with the standard deviation of SD=0.12 for accredited ones, 0.22 for the non-accredited and SD=0.20 for the all labs. Most of the laboratories got satisfactory z-score. On the other hand, non- accredited ones as N-AC3, N-AC15, N-AC13, N-AC6 (Table 4) and the only accredited laboratory AC8 (Table 5) were not able to pass the test for some calculation methods. These results indicated that the group type used for assigned value calculation relatively affect the z-score of the participants. When assigned value was determined based on the accreditation certificate of the participants, only limited number of non-accredited ones can't pass the test. However, if median of the all groups is considered in z-score calculation, more non-accredited laboratories can't succeed.

Table 3. Reported pH values for influent, effluent, mixed samples with estimated mixed value

Lab Code	Methods	*INF*	*EFF*	*MIX*	*EMV*
AC4	SM 4500 H+ B	7,50	7,17	7,50	7,33
AC5	SM 4500 H+	7,57	7,60	7,67	7,59
AC6	SM 4500 H+ B	7,49	7,65	7,66	7,57
AC7	SM 4500 H+ B	7,58	7,29	7,58	7,44
AC8	TS ISO 10523	7,22	7,11	7,60	7,17
AC9	TS ISO 10523	7,49	7,05	0,00	7,27
AC10	SM 4500 H+	7,38	7,19	7,31	7,29
AC11	TS EN ISO 10523	7,40	7,27	7,31	7,34
AC12	SM 4500 H+ B	7,33	7,04	7,42	7,19
N-AC1	Lange HQ40D	7,45	7,51	7,50	7,48
N-AC2	ThermoScientific	7,47	7,07	7,35	7,27
N-AC3	ThermoScientific	7,95	7,63	7,93	7,79
N-AC4	WTW Multi 3420	7,45	7,07	7,47	7,26
N-AC5	Hack Senson pH	7,55	7,42	7,44	7,49
N-AC6	Hach HQ11d	7,78	7,42	7,58	7,60
N-AC7	NR	7,70	7,41	7,66	7,56
N-AC8	Lange HQ30D	7,40	7,15	7,36	7,28
N-AC9	Louibond	7,67	7,34	7,52	7,51
N-AC10	WTW pH315i	7,28	7,11	7,33	7,20
N-AC11	Lange HQ40D	7,64	7,36	7,56	7,50
N-AC12	Lange HQ40D	7,91	7,93	7,85	7,92
N-AC13	Lange HQ40D	7,77	7,52	7,81	7,65
N-AC14	Lange Sension 1	7,47	7,21	7,27	7,34
N-AC15	Lange HQ40D	7,19	6,88	7,20	7,04
N-AC16	Lange HQ40D	7,41	7,09	7,43	7,25

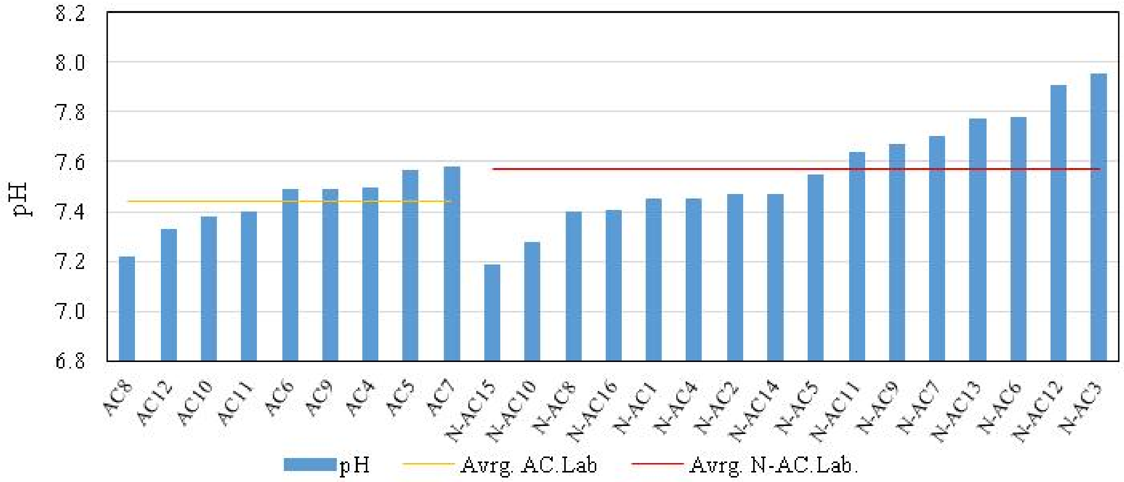

Figure 1. The reported pH values for the influent samples with the averages of the groups.

Table 4. Calculated z-scores of non-accredited laboratories for influent pH value.

LAB Code	$z = \frac{x - median}{MADe}$		$z = \frac{x - Avr}{MADe}$		$z = \frac{x - Avr}{SD}$	
	N-AC	All Lab	N-AC	All Lab	N-AC	All Lab
N-AC15	-1,49	-2,25	-1,76	-2,49	-1,74	-1,70
N-AC10	-1,07	-1,58	-1,34	-1,82	-1,33	-1,24
N-AC 8	-0,51	-0,68	-0,78	-0,92	-0,77	-0,63
N-AC 16	-0,47	-0,60	-0,74	-0,84	-0,73	-0,57
N-AC 1	-0,28	-0,30	-0,55	-0,54	-0,54	-0,37
N-AC 4	-0,28	-0,30	-0,55	-0,54	-0,54	-0,37
N-AC 2	-0,19	-0,15	-0,46	-0,39	-0,45	-0,27
N-AC 14	-0,19	-0,15	-0,46	-0,39	-0,45	-0,27
N-AC 5	0,19	0,45	-0,08	0,21	-0,08	0,14
N-AC 11	0,61	1,13	0,33	0,89	0,33	0,60
N-AC 9	0,75	1,35	0,47	1,11	0,47	0,76
N-AC 7	0,89	1,58	0,61	1,34	0,61	0,91
N-AC 13	1,21	2,10	0,94	1,86	0,93	1,27
N-AC 6	1,26	2,18	0,99	1,94	0,98	1,32
N-AC 12	1,86	3,15	1,59	2,91	1,57	1,99
N-AC 3	2,05	3,45	1,78	3,21	1,76	2,19

Table 5. Calculated z-scores of accredited laboratories for influent pH value.

LAB Code	$z = \frac{x - median}{MADe}$		$z = \frac{x - Avr}{MADe}$		$z = \frac{x - Avr}{SD}$	
	AC	All Lab	AC	All Lab	AC	All Lab
AC8	-2,03	-2,03	-1,65	-2,27	-1,87	-1,55
AC12	-1,20	-1,20	-0,83	-1,44	-0,93	-0,98
AC10	-0,83	-0,83	-0,45	-1,07	-0,51	-0,73
AC11	-0,68	-0,68	-0,30	-0,92	-0,34	-0,63
AC6	0,00	0,00	0,38	-0,24	0,42	-0,16
AC9	0,00	0,00	0,38	-0,24	0,42	-0,16
AC4	0,08	0,08	0,45	-0,17	0,51	-0,11
AC5	0,60	0,60	0,98	0,36	1,10	0,25
AC7	0,68	0,68	1,05	0,44	1,19	0,30

4.2. Conductivity Values and z-scores.

Conductivity is another electrochemical method commonly used to determine the quality of the wastewater effluents. Table 6 presents the methods used for analysis of conductivity, the reported measured values as well as EMV. The measured values do not vary substantially among the laboratories either accredited or non-accredited. The estimated mixed sample value is close to the reported value for the reported mixed sample. The standard deviation values are as follows, SD=0.33 µS for accredited laboratories, SD=0.43 µS for non-accredited ones and 0.39 for the all laboratories. Figure 2 indicates that averages of the laboratories for accredited and non-accredited ones. As it can been seen from the figure, the averages of the groups are close to each other. In addition, the variation in measured value of the non-accredited ones is stronger compared to that of accredited ones. Calculated z-scores by using different methods indicate that only laboratory N-AC7 fails. (Table 7). This result also shows that the variation in the measurements is not substantial. In other words, electrochemical methods could give consistent results. Therefore, the possibility of having satisfied z-score is high with this method.

Table 6. Reported conductivity values for influent, effluent, mixed samples with estimated mixed value (EMV).

Lab Code	Methods	*INF (µS)*	*EFF (µS)*	*MIX (µS)*	*EMV (µS)*
AC4	SM 2510 B	11.297	11.250	11.203	11.273
AC5	SM 2510 B	10.820	11.020	10.960	10.920
AC6	SM 2510 B	11.260	11.420	11.300	11.340
AC8	TS 9748	10.850	10.950	10.840	10.900
AC9	SM 2510 B	11.280	11.270	0.000	11.275
AC10	SM 2510	10.390	11.010	10.920	10.700
AC12	TS 9748	10.910	10.950	10.760	10.930
N-AC1	NR	11.030	11.160	11.120	11.095
N-AC2	NR	11.240	11.300	11.340	11.270
N-AC 3	NR	11.090	11.220	11.150	11.155
N-AC 4	NR	11.210	11.340	11.300	11.275
N-AC 6	WTW Multiline	11.340	11.500	11.420	11.420
N-AC 7	NR	10.020	10.410	10.370	10.215
N-AC 8	NR	11.340	11.530	11.410	11.435
N-AC 9	Hach HQ40D	11.270	11.330	11.270	11.300
N-AC 10	Hach HQ40D	10.560	10.770	10.720	10.665
N-AC 13	NR	11.600	11.650	11.600	11.625
N-AC 15	NR	10.820	10.860	10.900	10.840
N-AC 16	NR	10.690	10.810	10.870	10.750

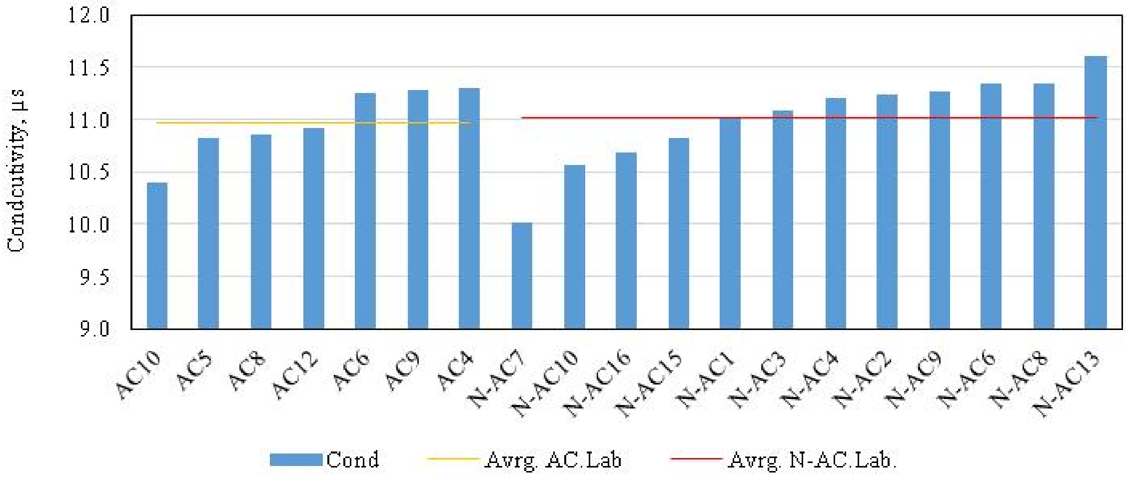

Figure 2. The reported conductivity values for the influent samples.

Table 7. Calculated z-scores for influent conductivity.

LAB Code	$z = \frac{x - median}{MADe}$		$z = \frac{x - Avr}{MADe}$		$z = \frac{x - Avr}{SD}$	
	AC- N-AC	All Lab	AC- N-AC	All Lab	AC- N-AC	All Lab
AC10	-1.00	-1.97	-1.12	-1.72	-1.75	-1.57
AC5	-0.17	-0.76	-0.29	-0.51	-0.46	-0.46
AC8	-0.12	-0.68	-0.24	-0.42	-0.37	-0.39
AC12	0.00	-0.51	-0.12	-0.26	-0.19	-0.23
AC6	0.68	0.48	0.56	0.73	0.86	0.67
AC9	0.71	0.53	0.59	0.79	0.92	0.72
AC4	0.75	0.58	0.63	0.83	0.97	0.76
N-AC7	-4.02	-3.01	-3.55	-2.76	-2.31	-2.52
N-AC 10	-2.10	-1.49	-1.63	-1.24	-1.06	-1.13
N-AC 16	-1.64	-1.13	-1.16	-0.88	-0.76	-0.80
N-AC 15	-1.17	-0.76	-0.70	-0.51	-0.46	-0.46
N-AC 1	-0.43	-0.17	0.04	0.08	0.03	0.07
N-AC 3	-0.21	0.00	0.26	0.25	0.17	0.23
N-AC 4	0.21	0.34	0.68	0.59	0.45	0.54
N-AC 2	0.32	0.42	0.79	0.67	0.51	0.61
N-AC 9	0.43	0.51	0.90	0.76	0.58	0.69
N-AC 6	0.68	0.70	1.15	0.95	0.75	0.87
N-AC 8	0.68	0.70	1.15	0.95	0.75	0.87
N-AC 13	1.60	1.44	2.07	1.69	1.35	1.54

4.3. Salinity Values and z-scores.

Salinity values of the influent, effluent and mixed sample were given in Table 8. The measured values are in the range of 5-35-6.50 ‰ for the all samples. The estimated mixed value is close to the value reported for the mixed samples. Figure 3 also shows the low variation in the reported values. The standard deviations are 0.49, 0.25, and 0.33 ‰ for the samples influent, effluent and mixed one. The low standard deviation value provides high number of z-score satisfaction for the participating laboratories. Only A12 and N7 cannot pass the comparison test. However, their z scores are substantially high which could reach up to 4.28 (A12) although the difference in the measured value among the laboratories is small. This result indicates that there is a problem with the equipments or methods used in the corresponding laboratories. The main problem with the equipment could be the calibration.

Table 8. Reported salinity values for influent, effluent, mixed samples with estimated mixed value (EMV).

Lab Code	Methods	*INF (‰)*	*EFF (‰)*	*MIX (‰)*	*EMV (‰)*
AC4	SM 2520 B	6.50	6.47	6.40	6.48
AC5	SM 2520 B	6.15	6.23	6.23	6.19
AC7	SM 2520 B	6.20	6.20	6.20	6.20
AC8	TS 8108	0.00	0.00	0.00	0.00
AC12	NR	5.35	5.37	5.27	5.36
N-AC1	NR	6.20	6.36	6.33	6.28
N-AC2	NR	6.40	6.40	6.40	6.40
N-AC3	NR	6.30	6.40	6.40	6.35
N-AC4	NR	6.40	6.40	6.40	6.40
N-AC6	NR	6.50	6.60	6.60	6.55
N-AC7	NR	5.67	5.88	5.81	5.78
N-AC8	NR	6.44	6.56	6.49	6.50
N-AC9	NR	6.42	6.53	6.45	6.48
N-AC10	NR	6.03	6.11	6.08	6.07
N-AC13	NR	6.63	6.64	6.60	6.64
N-AC15	NR	6.13	6.18	6.20	6.16
N-AC16	NR	6.23	6.12	6.23	6.18

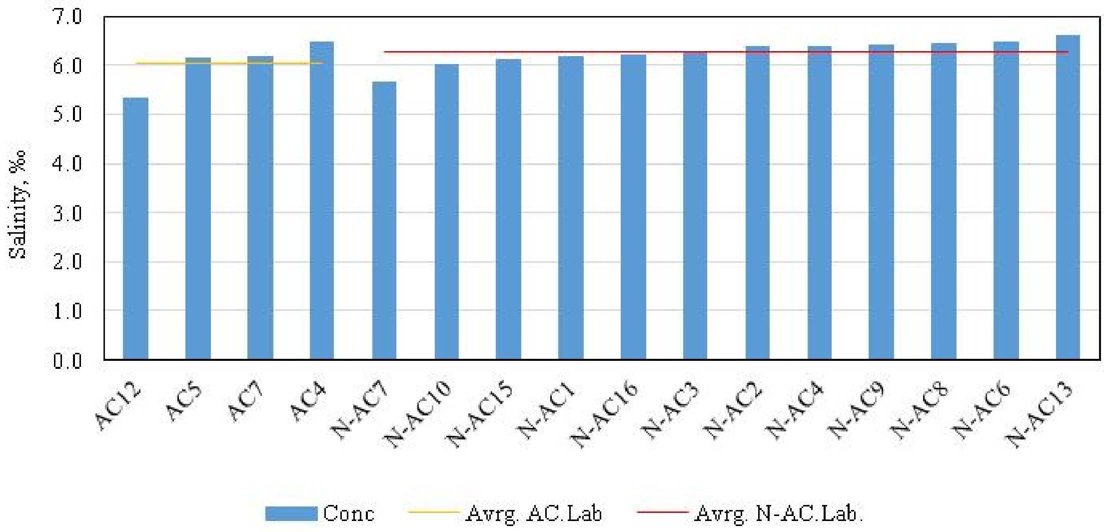

Figure 3. The reported salinity values for the influent samples.

Table 9. Calculated z-scores for salinity of influent sample.

LAB Code	$z = \frac{x - median}{MADe}$		$z = \frac{x - Avr}{MADe}$		$z = \frac{x - Avr}{SD}$	
	AC- N-AC	All Lab	AC- N-AC	All Lab	AC- N-AC	All Lab
AC12	-3.20	-4.28	-2.71	-4.08	-1.42	-2.68
AC5	-0.10	-0.54	0.39	-0.33	0.20	-0.22
AC7	0.10	-0.30	0.58	-0.10	0.31	-0.07
AC4	1.25	1.10	1.74	1.30	0.91	0.85
N-AC7	-3.40	-2.77	-3.05	-2.57	-2.40	-1.69
N-AC10	-1.60	-1.10	-1.25	-0.89	-0.98	-0.59
N-AC15	-1.10	-0.63	-0.75	-0.43	-0.59	-0.28
N-AC1	-0.75	-0.30	-0.40	-0.10	-0.31	-0.07
N-AC16	-0.60	-0.16	-0.25	0.04	-0.19	0.03
N-AC3	-0.25	0.16	0.10	0.37	0.08	0.24
N-AC2	0.25	0.63	0.60	0.83	0.48	0.55
N-AC4	0.25	0.63	0.60	0.83	0.48	0.55
N-AC9	0.35	0.72	0.70	0.92	0.55	0.61
N-AC8	0.45	0.82	0.80	1.02	0.63	0.67
N-AC6	0.75	1.10	1.11	1.30	0.87	0.85
N-AC13	1.40	1.70	1.76	1.90	1.38	1.25

5. CONCLUSION

It was shown that the nature of the analytical method could affect the z-score of the laboratories. pH, conductivity or salinity are the measurement based on electrochemical analytical methods. The influence of the other factors such as technical staff ability on the measurement may not be a factor in the z-score for these types of the measurements. The z-score calculations made on these measurements indicated that the possibility of having unsatisfactory result is low. The method used in z-score calculation does not essentially affect the z-score of the laboratory. In other words, it does not matter which z-score calculation is used, the lab with low performance will not pass the comparison test. Therefore, it could be advice to do only routine calibration of the equipment's rather that participating to proficiency tests.

REFERENCES

TS ISO 13528 (2015) Statistical methods for use in proficiency testing by interlaboratory comparisons, Turkish Standart Institute, Ankara, Turkey

TS EN ISO / IEC 17043 (2010) Conformity assessment – General requirements for proficiency testing, Turkish Standart Institute, Ankara, Turkey