Performance Report for Proficiency Testing

APLAC T104, Metals (Lead and Nickel) in Water

Nov 2016

Asia Pacific Laboratory Accreditation Cooperation

Summary

PT PROGRAM	**APLAC T104 (KOLAS PT 2016–18) (Heavy metals in water; Pb and Ni)**
OPERATING PERIOD	**June 20, 2016–July 15, 2016**
SCOPE OF ACCREDITION	**Section: Chemical test, Division: Water quality (2.021)**

□ Details of the proficiency testing (PT) program operation are as follows:

○ Number of participating laboratories

- Lead: 149 laboratories, Nickel: 144 laboratories

Lead → ISO/IEC 17025 Accreditation laboratories: 126

Nickel → ISO/IEC 17025 Accreditation laboratories: 122

○ Statistical analysis of the PT results are as follows:

- Performance assessment applied with z-score (standard deviation) of ISO 13528:2015

	Assigned value (mg/L)	Standard deviation (mg/L)	Standard uncertainty of the assigned value (mg/L)
Lead	0.030	0.001 8	0.000 2
Nickel	0.021	0.001 0	0.000 1

- Performance assessment results

Lead → Satisfactory: 112, Questionable: 6, Unsatisfactory: 31

Nickel → Satisfactory: 107, Questionable: 10, Unsatisfactory: 27

□ Production of PT program items is as follows:

○ Proficiency item development (K-Water)

- Items: Heavy metals (Lead and Nickel)
- Medium: Water
- Sample: 1 bottle (20 mL)

□ Test methods

- All standard methods can be used

□ Assessment of test results

- Algorithm A from Annex C.1 of ISO 13528:2015
- Assigned values: Results of participating laboratories obtained from the PT
- Standard deviation: Standard deviation of participating laboratories

Contents

1. Introduction

Proficiency testing is one of the methods for managing quality and guaranteeing test results, besides test capability assessment. As defined in the “Authorized laboratories accreditation system operation know-how” by the Korea Laboratory Accreditation Scheme (KOLAS), test laboratories should participate in a proficiency testing at least once every three years.

The Water Quality Research Center of K-water Institute (No. 7 in Korea) at the Korea Water Resources Corporation (K-water), a KS Q ISO/IEC 17043 requirement-based KOLAS proficiency test operating laboratories, implemented a proficiency program on the “heavy metals in water (Lead and Nickel)” in June-July 2016, which was intended for domestic and foreign international authorized test laboratories and laboratories that wished to participate. The criteria of Lead (Pb) in the drinking water is 0.010 mg/L, Korea. However, the criteria of Nickel (Ni) in water has been not established in Korea. This is the report describing the details of the overview of a proficiency testing program on heavy metals in water (Lead and Nickel), procedures, and the performance evaluation of participating laboratories.

2. Proficiency testing design and operation

2.1 Overview

The proficiency testing was conducted in June 20–July 15, 2016, for 26 days including the sample distribution day. Among the 177 applied laboratories, a total of 150 laboratories, 149 for Lead and 144 for Nickel, participated in this test (Table 1). In addition, among the result submitting laboratories, 23 from each item were not authorized by the accreditation scheme.

Table 1. Participating laboratories status

Category	Lead	Nickel
Applied laboratories (ISO/IEC 17025 Accreditation laboratories)	176 (148)	171 (144)
Laboratories that submitted results (participated) (ISO/IEC 17025 Accreditation laboratories)	149 (126)	144 (122)

2.2 Proficiency sample preparation

Samples for proficiency testing were prepared by K-water and distributed after testing their effectiveness, including homogeneity and stability.

(1) Concentration range selection

The concentration of the sample was decided considering usual analysis concentrations and abilities of testing equipment. The concentration range of the proficiency samples was set as follows (Table 2).

Table 2. Proficiency sample concentration

Lead	Nickel
(0.010–0.100) mg/L	(0.010–0.100) mg/L

(2) Sample preparation

Samples were prepared according to the standard solution preparation procedure and the method of KS I ISO 11885:2008, KS Q ISO Guide 30 (Table 3).

Table 3. Proficiency sample test method

Items	Test method	Detailed method	Quantification range
Lead	Inductively coupled plasma-mass spectrometry	ICP-MS	Above 0.000 1 mg/L
Nickel			Above 0.000 1 mg/L

(3) Effectiveness assessment of proficiency sample preparation

Homogeneity and short-term stability test were performed on the Basis of ISO Guide 35 for assessing the effectiveness of proficiency samples.

☐ Homogeneity assessment

The homogeneity tests were carried out on 12 samples selected randomly and each sample was analyzed twice. From the results obtained by the assessment of the homogeneity of proficiency samples using an ANOVA, a statistical analysis method, for Lead, the F ratio (0.462) was smaller than the F critical value (2.216), and for Nickel, the F ratio (1.888) was smaller than the F critical value (2.216), confirming that the proficiency samples are homogeneous. It was possible to ensure that they are sufficiently homogeneous to be used in the proficiency program.

☐ Stability assessment

The assessment of stability was performed according to KS Q ISO Guide 35. After the distribution of the samples taking into account the sample shipping period, as a result of assessing the stability of proficiency samples according to the number of days elapsed after the distribution and temperature change using an ANOVA (two-way analysis of variance), the stability of the proficiency samples is ensured. Also, as the difference with the result obtained from the homogeneity test (Lead: 0.000 2 mg/L, Nickel: 0.000 1 mg/L) is 0.3 times smaller than the target value for the standard deviation, we can confirm that stability is ensured according to ISO 13528:2015.

2.3 Sample distribution

A bottle of a mixed sample (20 mL) was provided to the participating laboratories, and a unique code number was given to each laboratory for the confidentiality of results. The participants diluted the sample 200 times for tests and were informed to submit test results without a separate conversion process (Table 4).

Table 4. Content for the distribution of samples

Preparation of samples (No.1–No.300)	Random selection of a mixed sample
	
Stable packing	Delivered by air freight
	

3. Statistical analysis and assessment

3.1 Data of participants

Table 5 shows the results and MU (standard measurement uncertainty) of the 150 participants:

Laboratories code	Lead		Nickel	
	Result (mg/L)	Standard measurement uncertainty (mg/L)	Result (mg/L)	Standard measurement uncertainty (mg/L)
M - 001	**0.030**	0.005	**0.020**	0.004
M - 004	**0.030**	0.004	**0.019**	0.002
M - 005	**0.030**	0.004	**0.021**	0.003
M - 006	**0.029**	0.006	**0.022**	0.003
M - 007	**0.031**	0.005	**0.021**	0.003
M - 008	**0.030**	0.0053	**0.021**	0.0023
M - 009	**0.035**	0.007	**0.013**	0.005
M - 010	**0.031**	0.005	**0.024**	0.003
M - 011	**0.032**	0.001	**0.021**	-
M - 016	**0.030**	0.001	**0.021**	0.001
M - 017	**0.030**	0.001	**0.020**	0.001
M - 018	**0.031**	0.004	**0.022**	0.004
M - 019	**0.125**	-	**0.029**	-
M - 021	**0.029**	-	**0.020**	-
M - 022	**0.016**	0.0005	**0.014**	0.0007
M - 024	**0.029**	-	**0.019**	-
M - 025	**0.027**	0.003	-	-

Laboratories code	Lead		Nickel	
	Result (mg/L)	Standard measurement uncertainty (mg/L)	Result (mg/L)	Standard measurement uncertainty (mg/L)
M - 026	**0.031**	-	**0.021**	-
M - 031	**6.025**	0.02	**3.850**	0.038
M - 032	**0.032**	0.0014	**0.022**	0.0001
M - 033	**0.038**	0.009	**0.021**	0.001
M - 035	**0.430**	0.0249	-	-
M - 042	**0.032**	0.0011	**0.020**	0.0006
M - 043	**0.031**	0.01	**0.020**	0.01
M - 044	**0.031**	-	-	-
M - 045	**0.029**	0.01	**0.020**	0.007
M - 046	**0.031**	0.001	**0.022**	0.001
M - 051	**0.020**	-	**0.030**	-
M - 055	**0.135**	-	**0.051**	-
M - 056	**0.024**	-	**0.031**	-
M - 058	**0.032**	0.005	**0.020**	0.004
M - 059	**0.029**	0.008	**0.020**	0.004
M - 060	**0.035**	0.0107	**0.020**	0.0066
M - 061	**0.03**	0.003	**0.016**	0.002
M - 062	**0.031**	0.002	**0.021**	0.002
M - 066	**0.027**	0.0001	**0.019**	0.0001
M - 074	**0.029**	0.0012	**0.021**	0.0025

Laboratories code	Lead		Nickel	
	Result (mg/L)	Standard measurement uncertainty (mg/L)	Result (mg/L)	Standard measurement uncertainty (mg/L)
M - 075	**0.029**	0.00001	**0.019**	0.00001
M - 077	**0.032**	0.018	**0.021**	0.0144
M - 078	**0.029**	0.004	**0.020**	0.0048
M - 085	**0.030**	0.00038	**0.020**	0.00035
M - 086	**0.031**	0.0027	**0.020**	0.0019
M - 073	**6.498**	0.377	**4.329**	0.647
M - 087	**0.030**	0.008	**0.020**	0.005
M - 088	**0.027**	0.0055	**0.021**	0.0033
M - 089	**0.030**	0.0091	**0.020**	0.0071
M - 090	**0.030**	0.008	**0.020**	0.005
M - 094	**0.031**	0.005	**0.020**	0.003
M - 095	**0.029**	0.006	**0.020**	0.004
M - 096	**0.029**	0.003	**0.020**	0.002
M - 097	**0.033**	0.004	**0.022**	0.002
M - 098	**0.032**	0.0016	**0.024**	0.0015
M - 099	**0.027**	0.0002	**0.018**	0.0001
M - 103	**0.031**	0.0035	**0.020**	0.0026
M - 105	**0.034**	0.0047	**0.022**	0.0013
M - 111	**0.025**	0.004	**0.020**	0.003
M - 112	**4.920**	-	**0.060**	-

Laboratories code	Lead		Nickel	
	Result (mg/L)	Standard measurement uncertainty (mg/L)	Result (mg/L)	Standard measurement uncertainty (mg/L)
M - 113	**0.027**	0.0047	**0.021**	0.0041
M - 114	**0.033**	0.002	**0.021**	0.009
M - 116	**0.030**	0.013	**0.022**	0.009
M - 117	**0.031**	0.009	**0.022**	0.007
M - 120	**0.027**	0.004	**0.020**	0.002
M - 121	**0.020**	0.002	**0.019**	0.002
M - 122	**0.019**	0.001	**0.015**	0.001
M - 128	**0.031**	0.0116	**0.021**	0.099
M - 129	**0.031**	0.006	**0.020**	0.004
M - 137	**0.031**	0.001	**0.019**	0.001
M - 140	**0.031**	0.00005	**0.021**	0.00005
M - 144	**6.473**	0.9917	**3.993**	0.5375
M - 147	**0.033**	0.003	**0.023**	0.002
M - 149	**0.030**	0.004	**0.020**	0.002
M - 150	**0.053**	0.04	**0.056**	0.07
M - 153	**0.021**	0.002	**0.019**	0.001
M - 154	**0.031**	0.01	**0.022**	0.01
M - 155	**0.025**	0.001	**0.015**	0.001
M - 156	**0.035**	0.002	**0.018**	0.001
M - 158	**0.030**	-	**0.020**	-

Laboratories code	Lead		Nickel	
	Result (mg/L)	Standard measurement uncertainty (mg/L)	Result (mg/L)	Standard measurement uncertainty (mg/L)
M - 159	**0.027**	-	**0.032**	-
M - 161	**3.487**	0.001	**5.580**	0.002
M - 162	**0.032**	-	**0.021**	-
M - 166	**0.035**	0.01	**0.020**	0.006
M - 167	**0.030**	0.001	**0.020**	0.0006
M - 168	**0.023**	0.001	**0.023**	0.001
M - 170	**0.087**	0.013	**0.068**	0.01
M - 171	**0.042**	0.002	**0.024**	0.002
M - 174	**0.031**	-	**0.021**	-
M - 175	**0.029**	0.007	-	-
M - 176	**0.030**	0.002	**0.021**	0.001
M - 178	-	-	**0.026**	0.005
M - 180	**0.058**	0.0012	**0.033**	0.0012
M - 184	**0.025**	0.0008	**0.020**	0.0006
M - 185	**0.031**	0.0004	**0.020**	0.0002
M - 186	**0.032**	0.003	**0.019**	0.002
M - 187	**0.032**	0.005	**0.020**	0.001
M - 188	**0.030**	0.004	**0.021**	0.002
M - 189	**0.030**	0.001	**0.022**	0.0024
M - 191	**0.031**	0.003	**0.021**	0.002

Laboratories code	Lead		Nickel	
	Result (mg/L)	Standard measurement uncertainty (mg/L)	Result (mg/L)	Standard measurement uncertainty (mg/L)
M - 192	**0.029**	0.003	**0.019**	0.002
M - 195	**0.031**	0.005	**0.020**	0.004
M - 196	**20.820**	4.372	**30.520**	6.715
M - 197	**0.033**	0.007	**0.022**	0.004
M - 198	**0.032**	0.0013	**0.022**	0.001
M - 199	**0.0328**	0.0033	**0.021**	0.0031
M - 200	**0.032**	0.0016	**0.021**	0.0015
M - 202	**0.031**	0.004	**0.020**	0.003
M - 203	**6.100**	0.2	**4.000**	0.2
M - 206	**0.031**	-	**0.022**	-
M - 207	**0.03**	0.0004	**0.021**	0.0007
M - 208	**0.031**	-	**0.020**	-
M - 209	**0.026**	0.002	**0.018**	0.002
M - 210	**0.029**	0.003	**0.022**	0.001
M - 211	**0.03**	0.000247	**0.020**	0.000252
M - 212	**0.020**	0.002	**0.029**	0.002
M - 213	**30.740**	0.3396	**20.010**	0.2952
M - 214	**0.030**	0.001	**0.021**	0.001
M - 215	**0.030**	0.000	**0.021**	0.000936
M - 216	**0.031**	0.003	**0.021**	0.002

Laboratories code	Lead		Nickel	
	Result (mg/L)	Standard measurement uncertainty (mg/L)	Result (mg/L)	Standard measurement uncertainty (mg/L)
M - 217	**0.031**	0.00079	**0.021**	0.00064
M - 219	**0.031**	-	**0.019**	-
M - 221	**0.030**	-	**0.021**	0.014
M - 222	**7.372**	-	**0.025**	-
M - 225	**6.944**	1.267	**3.802**	0.654
M - 226	**0.031**	-	**0.020**	-
M - 227	**0.030**	0.006	**0.021**	0.003
M - 230	**0.030**	0.0061	**0.021**	0.0036
M - 231	**0.032**	0.001	**0.021**	0.001
M - 234	**30.190**	4.739	**20.310**	3.088
M - 238	**0.028**	0.004	**0.020**	0.004
M - 239	**0.033**	0.005	**0.020**	0.003
M - 241	**0.029**	0.006	**0.021**	0.004
M - 242	**0.029**	0.005	**0.020**	0.004
M - 243	**0.029**	0.0059	**0.020**	0.004
M - 244	**0.03**	0.004	**0.020**	0.003
M - 245	**0.030**	0.003	**0.021**	0.003
M - 246	**0.029**	0.002	**0.020**	0.002
M - 247	**0.020**	-	**0.027**	0.001
M - 255	**0.030**	0.003	**0.021**	0.002

Laboratories code	Lead		Nickel	
	Result (mg/L)	Standard measurement uncertainty (mg/L)	Result (mg/L)	Standard measurement uncertainty (mg/L)
M - 258	**0.029**	0.005	**0.021**	0.0028
M - 264	**0.038**	0.008	**0.023**	0.004
M - 265	**0.031**	0.004	**0.024**	0.003
M - 267	**0.033**	0.004	**0.020**	0.003
M - 269	**0.032**	0.0032	**0.021**	0.003
M - 271	**0.020**	0.004	**0.019**	0.004
M - 272	**0.030**	0.004	**0.021**	0.004
M - 277	**0.032**	0.0005	**0.020**	0.0005
M - 284	**0.028**	0.003	**0.019**	0.002
M - 285	**0.032**	0.003	-	-
M - 287	**0.030**	0.001	**0.021**	0.001
M - 288	**0.029**	0.001	-	-
M - 289	**0.030**	0.002	**0.021**	0.001

* "-" : The participants did not submitted the result and/or MU data in this PT

3.2 Statistical analysis

For assessing the performance of this proficiency test, among the assigned value and standard deviation calculation methods suggested by ISO 13528:2015, the most common method was used, which is to set a consensus value (median) as the assigned value (x_{pt}), and the results obtained from the proficiency test (data obtained from one round of proficiency test) as the

standard deviation (σ_{pt}). We referred to algorithm A (robust analysis) in ISO 13528:2015 Annex C for the details of the calculation process.

According to ISO 13528:2015, Item 2 (a guideline for a limitation on the uncertainty of assigned values),

$$u_x \leq 0.3(\sigma_{pt})$$

In other words, the standard uncertainty of the assigned value (u_x) can be ignored only when it is smaller than 0.3 times the standard deviation (σ_{pt}), and it does not have to be included in the interpretation of proficiency test results.

In the case of this proficiency test, the assigned values and standard deviation calculation results of Lead and Nickel are shown in Table 6:

Table 6. Assigned values and standard deviation calculation results

Category	Lead	Nickel
Assigned value (mg/L)	0.030	0.021
Standard uncertainty of the assigned value* (mg/L)	0.000 2	0.000 1
Standard deviation (mg/L)	0.001 8	0.001 0
0.3 times the standard deviation (σ_{pt}) (mg/L)	0.000 5	0.000 3

*Standard uncertainty of the assigned value: A standard uncertainty, which occurs when a assigned value (x_{pt}) is set as the consensus value (median) of the proficiency test program participants without blunders

As shown in Table 6, the standard uncertainty of the Assigned value of both Lead and Nickel can be ignored as it is smaller than 0.3 times (σ_{pt}), and it does not need to be included in the interpretation of the proficiency test results. Accordingly, the z-score method, the most common

performance assessment method used for the performance assessment of participating laboratories, was applied.

$$z_i = \frac{x_i - x_{pt}}{\sigma_{pt}}$$

z : z-score

x_i : Test results of the participating laboratories

x_{pt} : Assigned value (applied with the consensus value of the participants)

σ_{pt}: Standard deviation used for performance assessment (robust standard deviation)

For the performance assessment of participating laboratories using the z-score, the following criteria are generally applied to the z value:

		$\lvert z \rvert$	$\leq$	2.0	Satisfactory
2.0	$<$	$\lvert z \rvert$	$<$	3.0	Questionable
3.0	$\leq$	$\lvert z \rvert$			Unsatisfactory

For more detailed information, please refer to ‘ISO 13528:2015’

For reference, for additional checking of validity in determining the consensus value of the participants as the assigned value, the assigned values and the average values of the homogeneity assessment, which were measured during the preparation of the proficiency samples, were compared. The results were significant as shown in Table 7:

Table 7. Comparison between the default and homogeneity average values

Items	Assigned value[*1] (mg/L)	Homogeneity average[*2] (mg/L)	Relative standard deviation (%)
Lead	0.031	0.031	0.824
Nickel	0.021	0.020	2.51

*Assigned value[*1]: Calculated value set as the consensus value of the participants (median)

*Homogeneity average[*2]: The average value obtained by the repeated measurement of the samples for homogeneity assessment when preparing the proficiency samples

4. Performance evaluation

4.1 Results for participants

Results for participants using z-score are given in Tables 8 ~ 11. In this study, 6 and 31 laboratories that tested Lead and Nickel were assessed as questionable and unsatisfactory, respectively.

For Lead, among the 149 participating laboratories, 6 were questionable, and 31 was unsatisfactory (Tables 8 and 10), and Figure 1 shows the z-score distribution by test laboratories.

For Nickel, among the 144 participating laboratories, 10 were questionable, and 27 were unsatisfactory (Tables 9 and 11). The z-score distribution by participated laboratories are shown in Figure 2.

Table 8. Result for Lead

Item	Satisfactory $\|z\| \leq 2.0$	Questionable $2.0 < \|z\| < 3.0$	Unsatisfactory $\|z\| \geq 3.0$	No. of participating laboratories
Lead	112	6	31	149

Table 9. Result for Nickel

Item	Satisfactory $\|z\| \leq 2.0$	Questionable $2.0 < \|z\| < 3.0$	Unsatisfactory $\|z\| \geq 3.0$	No. of participating laboratories
Nickel	107	10	27	144

Table 10. Result and z-score for Lead

Laboratories code	Result (mg/L)	z-score	Laboratories code	Result (mg/L)	z-score
M - 001	0.030	**-0.34**	M - 033	0.038	**3.52**
M - 004	0.030	**-0.34**	M - 035	0.430	**192.08**
M - 005	0.030	**-0.34**	M - 042	0.032	**0.63**
M - 006	0.029	**-0.82**	M - 043	0.031	**0.14**
M - 007	0.031	**0.14**	M - 044	0.031	**0.14**
M - 008	0.030	**-0.34**	M - 045	0.029	**-0.82**
M - 009	0.035	**2.07**	M - 046	0.031	**0.14**
M - 010	0.031	**0.14**	M - 051	0.020	**-5.39**
M - 011	0.032	**0.63**	M - 055	0.135	**50.19**
M - 016	0.030	**-0.34**	M - 056	0.024	**-3.23**
M - 017	0.030	**-0.34**	M - 058	0.032	**0.63**
M - 018	0.031	**0.14**	M - 059	0.029	**-0.82**
M - 019	0.125	**45.52**	M - 060	0.035	**1.83**
M - 021	0.029	**-0.82**	M - 061	0.03	**-0.34**
M - 022	0.016	**-7.27**	M - 062	0.031	**0.14**
M - 024	0.029	**-0.82**	M - 066	0.027	**-1.59**

M - 025	0.027	**-1.78**	M - 073	6.498	**3114.97**
M - 026	0.031	**0.29**	M - 074	0.029	**-0.96**
M - 031	6.025	**2887.15**	M - 075	0.029	**-0.82**
M - 032	0.032	**0.63**	M - 077	0.032	**0.63**

Laboratories code	Result (mg/L)	z-score	Laboratories code	Result (mg/L)	z-score
M - 078	0.029	**-0.82**	M - 117	0.031	**0.14**
M - 085	0.030	**-0.24**	M - 120	0.027	**-1.78**
M - 086	0.031	**-0.10**	M - 121	0.020	**-5.15**
M - 087	0.030	**-0.34**	M - 122	0.019	**-5.64**
M - 088	0.027	**-1.59**	M - 128	0.031	**0.14**
M - 089	0.030	**-0.24**	M - 129	0.031	**0.00**
M - 090	0.030	**-0.34**	M - 137	0.031	**0.14**
M - 094	0.031	**0.14**	M - 140	0.031	**0.15**
M - 095	0.029	**-0.82**	M - 144	6.473	**3102.93**
M - 096	0.029	**-0.82**	M - 147	0.033	**1.11**
M - 097	0.033	**1.11**	M - 149	0.030	**-0.34**
M - 098	0.032	**0.58**	M - 150	0.053	**10.74**
M - 099	0.027	**-1.78**	M - 153	0.021	**-4.67**
M - 103	0.031	**0.19**	M - 154	0.031	**0.14**
M - 105	0.034	**1.73**	M - 155	0.025	**-2.75**
M - 111	0.025	**-2.75**	M - 156	0.035	**2.07**

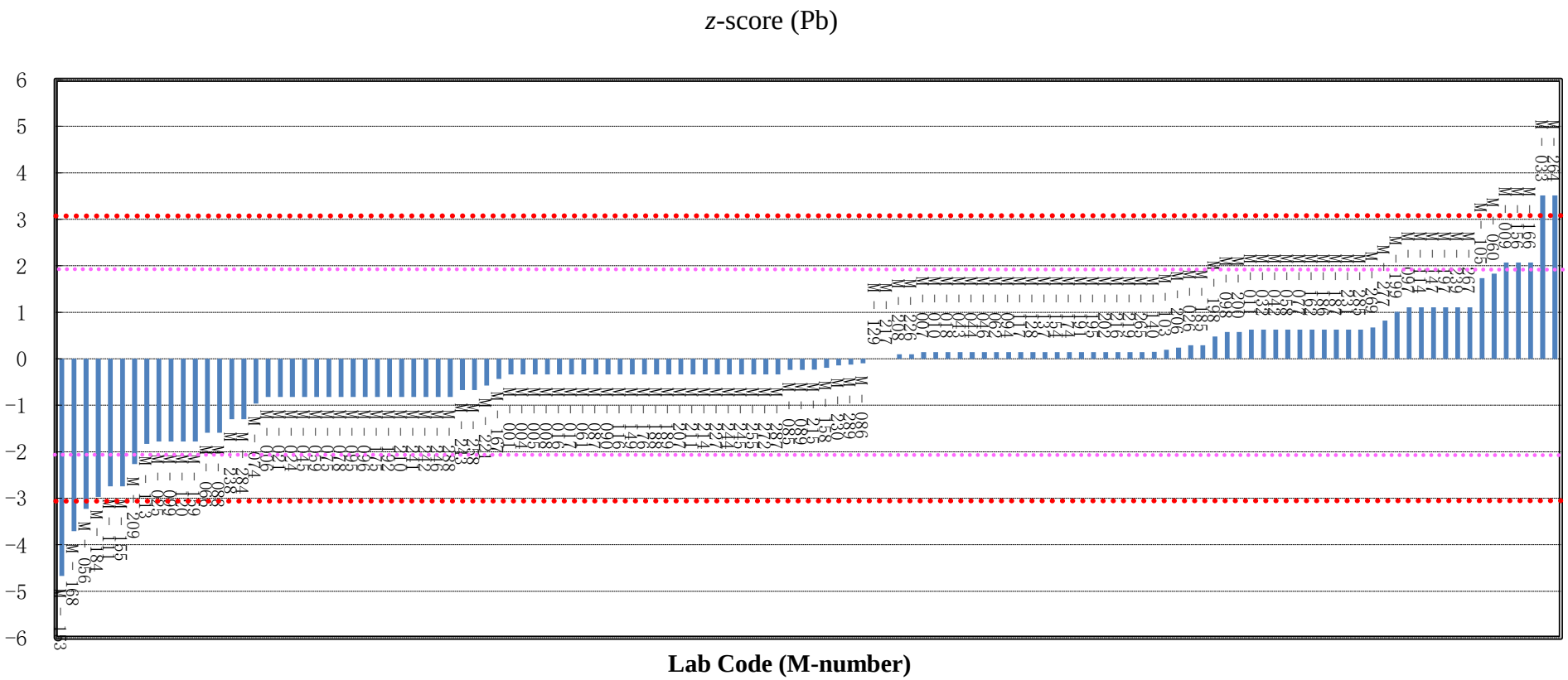
M - 112	4.920	**2354.93**	M - 158	0.030	**-0.19**
M - 113	0.027	**-1.83**	M - 159	0.027	**-1.78**
M - 114	0.033	**1.11**	M - 161	3.487	**1664.72**
M - 116	0.030	**-0.34**	M - 162	0.032	**0.63**

Laboratories code	Result (mg/L)	z-score	Laboratories code	Result (mg/L)	z-score
M - 166	0.035	**2.07**	M - 198	0.032	**0.48**
M - 167	0.030	**-0.43**	M - 199	0.0328	**1.01**
M - 168	0.023	**-3.71**	M - 200	0.032	**0.58**
M - 170	0.087	**27.12**	M - 202	0.031	**0.14**
M - 171	0.042	**5.44**	M - 203	6.100	**2923.27**
M - 174	0.031	**0.14**	M - 206	0.031	**0.24**
M - 175	0.029	**-0.82**	M - 207	0.03	**-0.34**
M - 176	0.030	**-0.34**	M - 208	0.031	**0.10**
M - 180	0.058	**13.29**	M - 209	0.026	**-2.26**
M - 184	0.025	**-2.97**	M - 210	0.029	**-0.82**
M - 185	0.031	**0.29**	M - 211	0.03	**-0.34**
M - 186	0.032	**0.63**	M - 212	0.020	**-5.15**
M - 187	0.032	**0.63**	M - 213	30.740	**14791.11**
M - 188	0.030	**-0.34**	M - 214	0.030	**-0.34**
M - 189	0.030	**-0.34**	M - 215	0.030	**-0.23**
M - 191	0.031	**0.14**	M - 216	0.031	**0.14**

M - 192	0.029	**-0.82**	M - 217	0.031	**0.00**
M - 195	0.031	**0.14**	M - 219	0.031	**0.14**
M - 196	20.820	**10013.15**	M - 221	0.030	**-0.58**
M - 197	0.033	**1.11**	M - 222	7.372	**3535.93**

Laboratories code	Result (mg/L)	z-score	Laboratories code	Result (mg/L)	z-score
M - 225	6.944	**3329.79**	M - 255	0.030	**-0.34**
M - 226	0.031	**0.10**	M - 258	0.029	**-0.67**
M - 227	0.030	**-0.34**	M - 264	0.038	**3.52**
M - 230	0.030	**-0.14**	M - 265	0.031	**0.14**
M - 231	0.032	**0.63**	M - 267	0.033	**1.11**
M - 234	30.190	**14526.20**	M - 269	0.032	**0.67**
M - 238	0.028	**-1.30**	M - 271	0.020	**-5.15**
M - 239	0.033	**1.11**	M - 272	0.030	**-0.34**
M - 241	0.029	**-0.82**	M - 277	0.032	**0.82**
M - 242	0.029	**-0.82**	M - 284	0.028	**-1.30**
M - 243	0.029	**-0.67**	M - 285	0.032	**0.63**
M - 244	0.03	**-0.34**	M - 287	0.030	**-0.34**
M - 245	0.030	**-0.34**	M - 288	0.029	**-0.82**
M - 246	0.029	**-0.82**	M - 289	0.030	**-0.12**
M - 247	0.020	**-5.15**			

Figure 1. z-score distribution for Lead



* The 25 laboratories (M-022, M-122, M-051, M-121, M-212, M-247, M-271, M-171, M-150, M-180, M-170, M-019, M-055, M-035, M-161, M-112, M-031, M-203, M-144, M-073, M-225, M-222, M-196, M-234, M-213) are excluded from the graph as it was judged to be an outlier from outlier verification in this PT program

Table 11. Results and z-score for Nickel

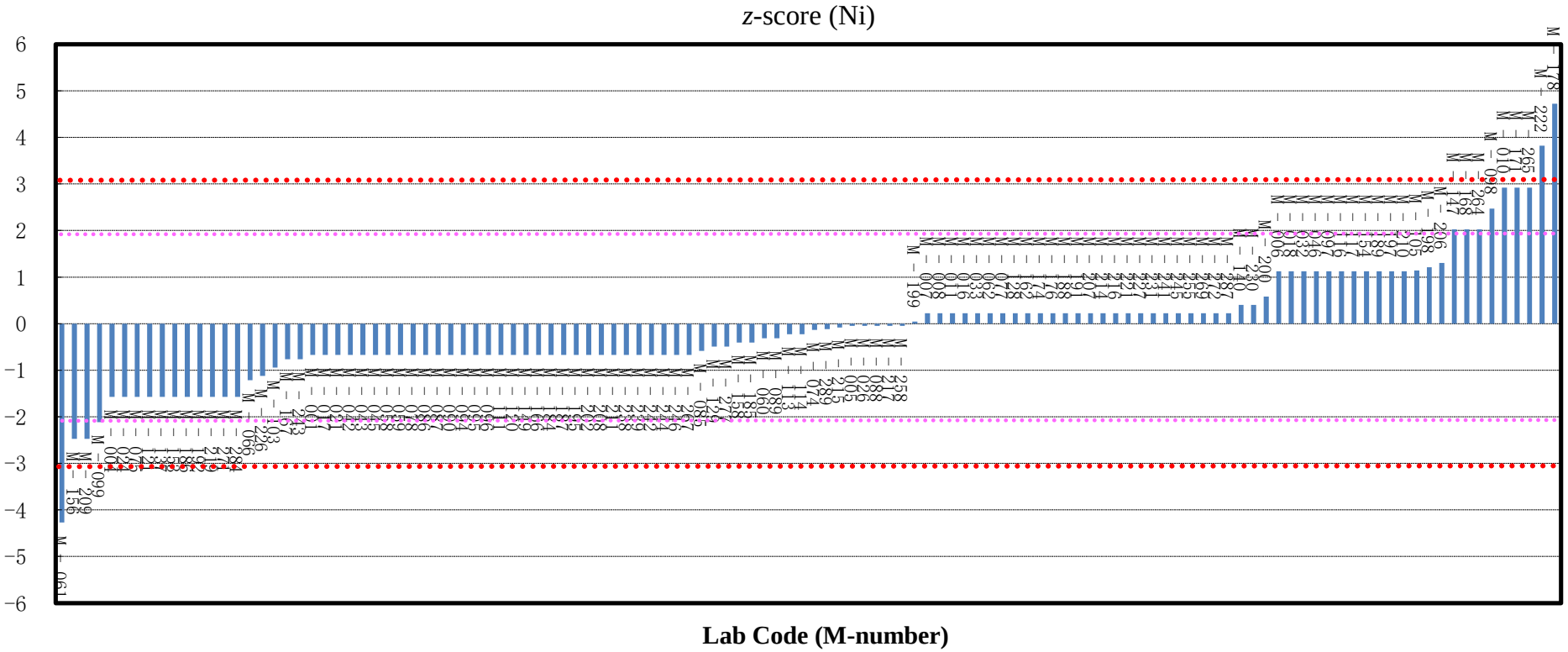
Laboratories code	Result (mg/L)	z-score	Laboratories code	Result (mg/L)	z-score
M - 001	0.020	**-0.67**	M - 042	0.020	**-0.67**
M - 004	0.019	**-1.57**	M - 043	0.020	**-0.67**
M - 005	0.021	**-0.04**	M - 045	0.020	**-0.67**
M - 006	0.022	**1.12**	M - 046	0.022	**1.12**
M - 007	0.021	**0.22**	M - 051	0.030	**8.14**
M - 008	0.021	**0.22**	M - 055	0.051	**27.02**
M - 009	0.013	**-6.97**	M - 056	0.031	**9.22**
M - 010	0.024	**2.92**	M - 058	0.020	**-0.67**
M - 011	0.021	**0.22**	M - 059	0.020	**-0.67**
M - 016	0.021	**0.22**	M - 060	0.020	**-0.31**
M - 017	0.020	**-0.67**	M - 061	0.016	**-4.27**
M - 018	0.022	**1.12**	M - 062	0.021	**0.22**
M - 019	0.029	**7.06**	M - 066	0.019	**-1.21**
M - 021	0.020	**-0.67**	M - 073	4.329	**3873.45**
M - 022	0.014	**-5.98**	M - 074	0.021	**-0.13**
M - 024	0.019	**-1.57**	M - 075	0.019	**-1.57**
M - 026	0.021	**-0.04**	M - 077	0.021	**0.22**
M - 031	3.850	**3442.80**	M - 078	0.020	**-0.67**
M - 032	0.022	**1.12**	M - 085	0.020	**-0.58**
M - 033	0.021	**0.22**	M - 086	0.020	**-0.67**

Laboratories code	Result (mg/L)	z-score	Laboratories code	Result (mg/L)	z-score
M - 087	0.020	**-0.67**	M - 122	0.015	**-5.17**
M - 088	0.021	**-0.04**	M - 128	0.021	**0.22**
M - 089	0.020	**-0.31**	M - 129	0.020	**-0.49**
M - 090	0.020	**-0.67**	M - 137	0.019	**-1.57**
M - 094	0.020	**-0.67**	M - 140	0.021	**0.40**
M - 095	0.020	**-0.67**	M - 144	3.993	**3571.36**
M - 096	0.020	**-0.67**	M - 147	0.023	**2.02**
M - 097	0.022	**1.12**	M - 149	0.020	**-0.67**
M - 098	0.024	**2.47**	M - 150	0.056	**31.69**
M - 099	0.018	**-2.11**	M - 153	0.019	**-1.57**
M - 103	0.020	**-0.94**	M - 154	0.022	**1.12**
M - 105	0.022	**1.14**	M - 155	0.015	**-5.17**
M - 111	0.020	**-0.67**	M - 156	0.018	**-2.47**
M - 112	0.060	**35.29**	M - 158	0.020	**-0.40**
M - 113	0.021	**-0.22**	M - 159	0.032	**10.11**
M - 114	0.021	**-0.22**	M - 161	5.580	**4998.20**
M - 116	0.022	**1.12**	M - 162	0.021	**0.22**
M - 117	0.022	**1.12**	M - 166	0.020	**-0.67**
M - 120	0.020	**-0.67**	M - 167	0.020	**-0.76**
M - 121	0.019	**-1.57**	M - 168	0.023	**2.02**

Laboratories code	Result (mg/L)	z-score	Laboratories code	Result (mg/L)	z-score
M - 170	0.068	**42.48**	M - 202	0.020	**-0.67**
M - 171	0.024	**2.92**	M - 203	4.000	**3577.66**
M - 174	0.021	**0.22**	M - 206	0.022	**1.30**
M - 176	0.021	**0.22**	M - 207	0.021	**0.22**
M - 178	0.026	**4.72**	M - 208	0.020	**-0.67**
M - 180	0.033	**10.56**	M - 209	0.018	**-2.47**
M - 184	0.020	**-0.67**	M - 210	0.022	**1.12**
M - 185	0.020	**-0.40**	M - 211	0.020	**-0.67**
M - 186	0.019	**-1.57**	M - 212	0.029	**7.42**
M - 187	0.020	**-0.67**	M - 213	20.010	**17971.90**
M - 188	0.021	**0.22**	M - 214	0.021	**0.22**
M - 189	0.022	**1.12**	M - 215	0.021	**-0.08**
M - 191	0.021	**0.22**	M - 216	0.021	**0.22**
M - 192	0.019	**-1.57**	M - 217	0.021	**-0.04**
M - 195	0.020	**-0.67**	M - 219	0.019	**-1.57**
M - 196	30.520	**27421.22**	M - 221	0.021	**0.22**
M - 197	0.022	**1.12**	M - 222	0.025	**3.82**
M - 198	0.022	**1.21**	M - 225	3.802	**3399.64**
M - 199	0.021	**0.04**	M - 226	0.020	**-1.12**
M - 200	0.021	**0.58**	M - 227	0.021	**0.22**

Laboratories code	Result (mg/L)	z-score	Laboratories code	Result (mg/L)	z-score
M - 230	0.021	**0.40**	M - 255	0.021	**0.22**
M - 231	0.021	**0.22**	M - 258	0.021	**-0.04**
M - 234	20.310	**18241.63**	M - 264	0.023	**2.02**
M - 238	0.020	**-0.67**	M - 265	0.024	**2.92**
M - 239	0.020	**-0.67**	M - 267	0.020	**-0.67**
M - 241	0.021	**0.22**	M - 269	0.021	**0.22**
M - 242	0.020	**-0.67**	M - 271	0.019	**-1.57**
M - 243	0.020	**-0.76**	M - 272	0.021	**0.22**
M - 244	0.020	**-0.67**	M - 277	0.020	**-0.49**
M - 245	0.021	**0.22**	M - 284	0.019	**-1.57**
M - 246	0.020	**-0.67**	M - 287	0.021	**0.22**
M - 247	0.027	**5.62**	M - 289	0.021	**-0.12**

Figure 2. z-score distribution for Nickel

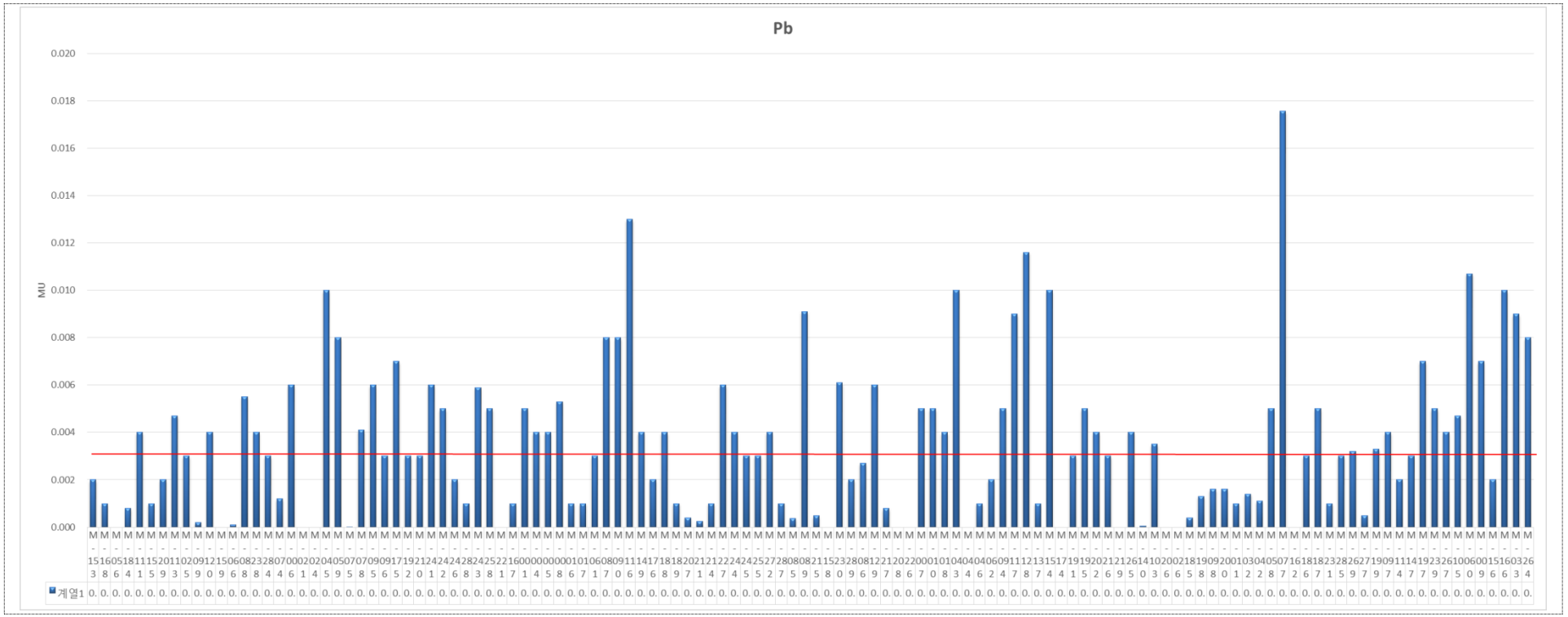


* The 24 laboratories (M - 009, M - 019, M - 022, M - 031, M - 051, M - 055, M - 056, M - 073, M - 112, M - 122, M - 144, M - 150, M - 155, M - 159, M - 161, M - 170, M - 180, M - 196, M - 203, M - 212, M - 213, M - 225, M - 234, M - 247) are excluded from the graph as they were judged to be outliers from outlier verification in this PT program.

4.2 Results and MU (Measurement uncertainty)

Results and measurements uncertainty are given in Figures 3 and 4.

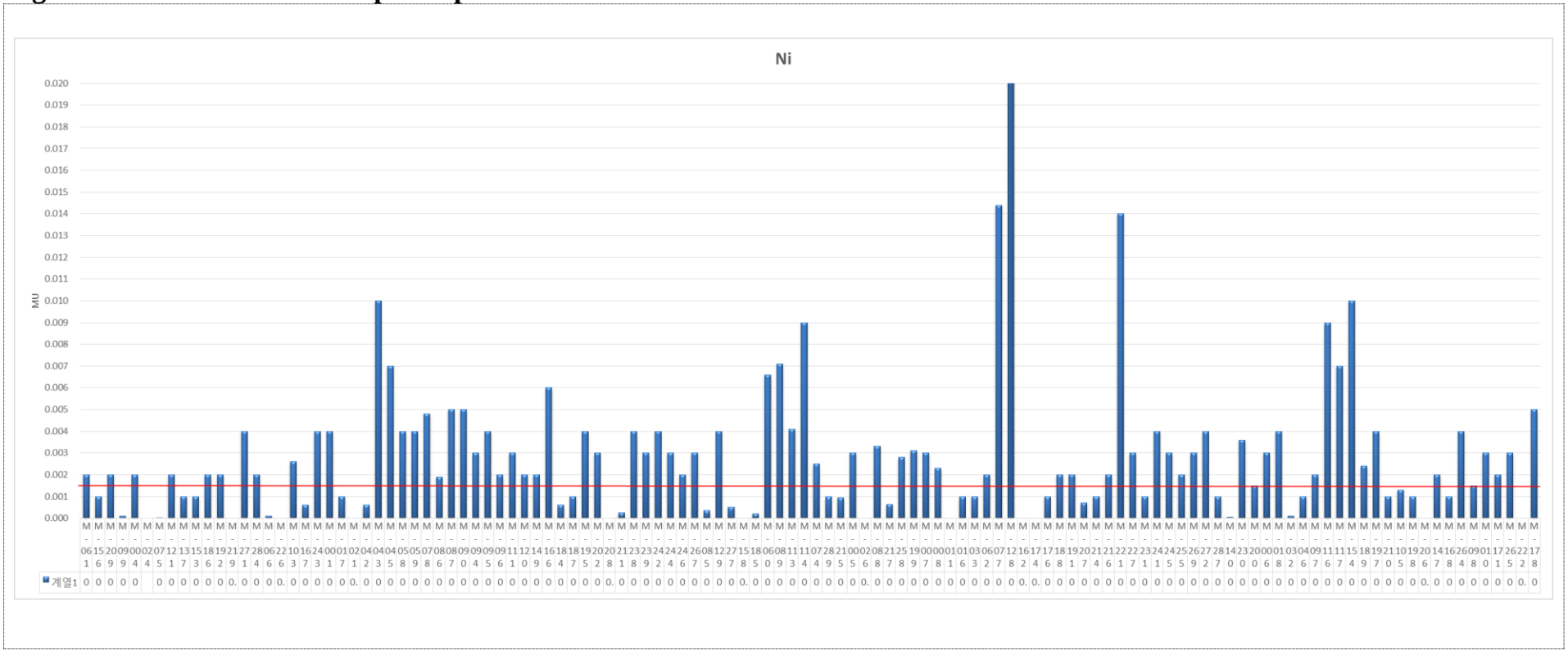
Figure 3. Results and MU of participants for Lead



* MU: Measurement uncertainty

Laboratories which did not submit MU or had significantly larger MU values compared to Umax are recommended to self-evaluate affecting factors. In addition, the solid-line of upper bound is estimated as Umax, 0.002 7 (1.5×s*), based on ISO 13528:2015 (9.8.4).

Figure 4. Results and MU of participants for Nickel



* MU: Measurement uncertainty

Laboratories which did not submit MU or had significantly larger MU values compared to Umax are recommended to self-evaluate affecting factors. In addition, the solid-line of upper bound is estimated as Umax, 0.001 6 (1.5×s*), based on ISO 13528:2015 (9.8.4).

4.3 Test method and instrument

Most laboratories are using their national test methods as a routine method. The methods are classified into 3 majors; inductively coupled plasma-optical emission spectrometer (ICP-OES), inductively coupled plasma-mass spectrometer (ICP-MS), and atomic absorption spectroscopy (AAS). As compared to the result obtained from the performance assessment according to the use of the test equipment, for Lead, the majority of 3 instruments was satisfactory (72~75%), where no difference was observed to be caused by equipment (Table 12). However, the 8 laboratories that used other instruments were shown about 50% questionable or unsatisfactory in this program.

Table 12. Comparison of test methods for Lead

Test method	No. of laboratories	Laboratories code
Total	149	
ICP-OES	39 (11)	M - 010, M - 017, M - 021, M - 025, M - 026, M - 043, M - 051, M - 056, M - 061, M - 073, M - 078, M - 090, M - 097, M - 098, M - 111, M - 114, M - 116, M - 120, M - 121, M - 122, M - 153, M - 154, M - 161, M - 162, M - 166, M - 167, M - 171, M - 185, M - 197, M - 202, M - 203, M - 217, M - 234, M - 246, M - 247, M - 255, M - 258, M - 265, M - 272
ICP-MS	65 (6)	M - 001, M - 004, M - 005, M - 006, M - 007, M - 008, M - 011, M - 016, M - 018, M - 024, M - 031, M - 058, M - 066, M - 074, M - 075, M - 077, M - 085, M - 086, M - 087, M - 089, M - 094, M - 095, M - 096, M - 099, M - 103, M - 113, M - 128, M - 129, M - 137, M - 140, M - 144, M - 147, M - 149, M - 158, M - 168, M - 174, M - 175, M - 176, M - 191, M - 192, M - 195, M - 196, M - 198, M - 200, M - 207, M - 208, M - 209, M - 211, M - 212, M - 213, M - 214, M - 215, M - 216, M - 219, M - 226, M - 227, M - 230, M - 243, M - 244, M - 267, M - 284, M - 285, M - 287, M - 288, M - 289
AAS	37 (10)	M - 009, M - 019, M - 022, M - 033, M - 035, M - 042, M - 044, M - 046, M - 060, M - 062, M - 105, M - 117, M - 150, M - 155, M - 156, M - 159, M - 180, M - 186, M - 187, M - 188, M - 189, M - 199, M - 206, M - 210, M - 221, M - 222, M - 225, M - 231, M - 238, M - 239, M - 241, M - 242, M - 245, M - 264, M - 269,

		M - 271, M - 277
Etc.	8 (4)	M - 032, M - 045, M - 055, M - 059, M - 088, M - 112, M – 170, M - 184

* Unsatisfactory laboratory (31 labs) : M – 019, M – 022, M – 031, M – 033, M – 035, M – 051, M – 055, M – 056, M – 073, M – 112, M – 121, M – 122, M – 144, M – 150, M – 153, M – 161, M – 168, M – 170, M – 171, M – 180, M – 184, M – 196, M – 203, M – 212, M – 213, M – 222, M – 225, M – 234, M – 247, M – 264, M – 271

For Nickel, the majority of participating laboratories (> 90%) used to 3 instruments, ICP-OES, ICP-MS and AAS. The most used technique was ICP-MS (62 labs, 43%). This technique also provided satisfactory results for 90% of the results provided. ICP-OES and AAS which satisfactory results for 77% and 71% of the results provided (Table 13).

Table 13. Comparison of test methods for Nickel

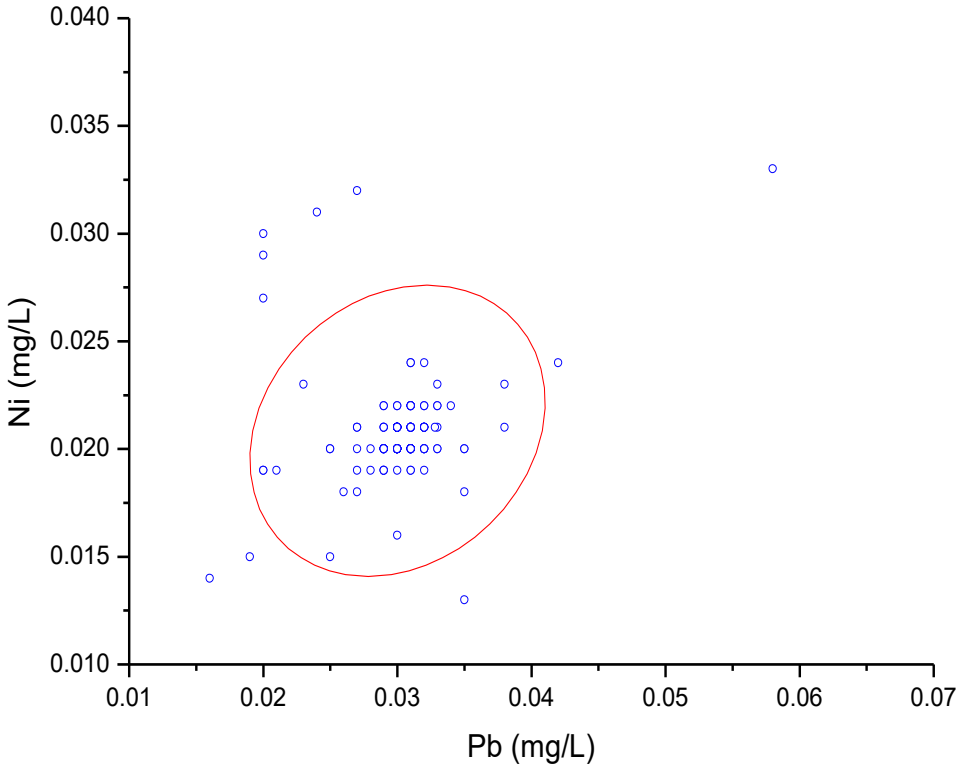
Test method	No. of laboratories	Laboratories code
Total	144	
ICP-OES	39 (9)	M - 010, M - 017, M - 021, M - 026, M - 043, M - 051, M - 056, M - 061, M - 073, M - 078, M - 090, M - 097, M - 098, M - 111, M - 114, M - 116, M - 120, M - 121, M - 122, M - 153, M - 154, M - 161, M - 162, M - 166, M - 167, M - 171, M - 185, M - 197, M - 202, M - 203, M - 210, M - 217, M - 234, M - 246, M - 247, M - 255, M - 258, M - 265, M - 272
ICP-MS	62 (5)	M - 001, M - 004, M - 005, M - 006, M - 007, M - 008, M - 011, M - 016, M - 018, M - 024, M - 031, M - 058, M - 066, M - 074, M - 075, M - 077, M - 085, M - 086, M - 087, M - 089, M - 094, M - 095, M - 096, M - 099, M - 103, M - 113, M - 128, M - 129, M - 137, M - 140, M - 144, M - 147, M - 149, M - 158, M - 168, M - 174, M - 176, M - 191, M - 192, M - 195, M - 196, M - 198, M - 200, M - 207, M - 208, M - 209, M - 211, M - 212, M - 213, M - 214, M - 215, M - 216, M - 219, M - 226, M - 227, M - 230, M - 243, M - 244, M - 267, M - 284, M - 287, M - 289

AAS	35 (10)	M - 009, M - 019, M - 022, M - 033, M - 042, M - 046, M - 060, M - 062, M - 105, M - 117, M - 150, M - 155, M - 156, M - 159, M - 178, M - 180, M - 186, M - 187, M - 188, M - 189, M - 199, M - 206, M - 221, M - 222, M - 225, M - 231, M - 238, M - 239, M - 241, M - 242, M - 245, M - 264, M - 269, M - 271, M - 277
Etc.	8 (3)	M - 045, M – 184, M - 032, M - 055, M - 059, M - 088, M - 112, M - 170

* Unsatisfactory laboratories (27 labs): M – 009, M – 019, M – 022, M – 031, M – 051, M – 055, M – 056, M – 061, M – 073, M – 112, M – 122, M – 144, M – 150, M – 155, M – 159, M – 161, M – 170, M – 178, M – 180, M – 196, M – 203, M – 212, M – 213, M – 222, M – 225, M – 234, M – 247

Figure 5 shows the distribution of Youden plot, Ni against Pb. Satisfactory result of both of them was achieved by 114 of 143 participants (about 80%) in the PT. This could be indicated that between compounds differences were probably not significant in the PT. The outlier 29 participants (M - 009, M - 019, M - 022, M - 031, M - 051, M - 055, M - 056, M - 073, M - 112, M - 122, M - 144, M - 150, M - 155, M - 156, M - 161, M - 168, M - 170, M - 171, M - 180, M - 196, M - 203, M - 209, M - 212, M - 213, M - 222, M - 225, M - 234, M – 247, and M – 264) are shown in the Figure 5. These participants are needed self-evaluate affecting some factors.

Figure 5. The result of Youden plot for Ni against Pb in water



5. Conclusions

As a proficiency test assessment result, the test laboratories that were assessed as questionable or unsatisfactory need to conduct a causal analysis, including managerial and technical system internal audits, reference materials, glassware, equipment checkup and correction, test procedure review, tester training, and continuous participation in proficiency tests of relevant areas, to promote efforts towards continuous improvement and preventive measures for performance improvement. Also, although the result was satisfactory, the laboratories exhibiting a broad range of measurement uncertainty need to consider causal analysis and improvement, such as reference materials, glassware, equipment checkup and correction, and test procedure review.

6. References

1. ISO Guide 35, Reference materials– general and statistical principles of certification

2. ISO 13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparison

APPENDIX

The document of instruction for APLAC T104 program, including the result sheet.

Asia Pacific Laboratory Accreditation Cooperation

(APLAC)

Proficiency Testing Programme

Instructions to Participating Laboratories

Trace Elements in Drinking Water

(Heavy metals; Lead and Nickel)

2016. May

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All laboratories participating in this proficiency testing program shall be fully aware of the following notices before measuring the proficiency testing samples.

1. Introduction

1.1 The purpose of this Proficiency Testing (PT) is to monitor the capabilities of the participating laboratories to perform water quality analysis and to enhance their quality assurance of measurements.

1.2 This proficiency testing is composed of testing heavy metals (Pb, Ni) in water.

2. Responsibilities

K-water (Water Quality Research Center) is responsible for preparing, packaging and dispatching samples, collecting test results from participating laboratories, conducting statistical analyses of the data, handling participants' queries and issuing final reports. K-water is the proficiency testing provider accredited by KOLAS on the basis of ISO/IEC 17043.

3. Participation to this program

3.1 The participating laboratories shall be nominated by the accreditation body and accepted the coordinator.

- The participation is free of charge

3.2 **The term of testing: June 13th to July 15th**

4. Proficiency testing sample

4.1 Information about PT sample

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One sample (20 mL) will be provided to the participants. Participating laboratories will be given one sample bottle labeled APLAC T104 (KOLAS PT-2016-18) from K-water. The bottle contains about 20 mL of a transparent and colorless mixture including two heavy metals (Pb, Ni) in water. This concentrate is preserved with 1% nitric acid. The concentrate can be stored at room temperature. New sample will be replaced for any damaged claims.

Please TEST after 200 TIMES DILUTION.

Table 1. The final concentration range.

Item / Unit	Lead (Pb)	Nickel (Ni)	Note
mg/L	0.010 ~ 0.100	0.010 ~ 0.100	Result of 200 times dilution

4.2 Receipt of the sample

The sample will be sent by air freight. Once the sample is received, please complete the attached ***"RECEIPT FORM"*** and then **fax (+82-42-629-2099) or e-mail (yun-skim@kwater.or.kr, awesome40@kwater.or.kr) within 3 days of receipt.**

5. Test

5.1 Preparation

Proper dilution procedure is as follows:

- Fill up a 200 mL class A volumetric flask with about 120 mL of 1% nitric acid.
- Add 1.0 mL of the provided sample to the flask.
- Fill the flask with 1% nitric acid solution to exactly 200 mL.
- Use the sample as a final analytical sample.

5.2 Test conditions

Please complete the testing as soon as possible after open the sample.

All standard methods for Lead and Nickel in water can be used.

(Recommend participants' usual test method.)

Note the test method and equipment used. If you are using Standard Methods for the Examination of Water and Wastewater 22nd edition 3125, you would report test method: Determination of metals by inductively coupled plasma-mass spectrometry (ICP-MS).

5.3 Laboratory safety

The sample should be handled in a laboratory. The analyst should have experience in handling, disposing of, and applying appropriate testing methods. Safety devices (safety goggles, hood system, etc.) should be fully equipped. Responsibility for the safe use of these products rests entirely with the buyer and/or user. Material Safety Data Sheets (MSDS) for the sample are available upon request.

6. Submission of results

Participants should submit their results electronically by **fax (+82-42-629-2099) or e-mail (yunskim@kwater.or.kr, awesome40@kwater.or.kr)** before the deadline **(July 15th, 2016)**. Results submitted after the deadline will not be accepted. Under no circumstances, corrections or adjustments of the analytical data will be accepted after submission.

** Participants should be aware that all submitted results are considered to be final and accordingly such data and units should be thoroughly checked before submission.*

7. Assigned Value and Performance Assessment

There is a way of performance assessment.

z-score with the robust mean

The assigned value for the test material used in the round of this proficiency testing scheme is the robust mean of the results reported by all the participants in the round. Evaluation of the Performance with ISO 13528:2015 in reference, z-scores will be applied to evaluate the test results that given by the participants, as following:

$$z_i = \frac{x_i - x_{pt}}{\sigma_{pt}}$$

Where x_i is the measurement value of the participant, x_{pt} is the robust mean (assigned value), σ_{pt} is the standard deviation for proficiency assessment.

The assigned value (x_{pt}) and SDPA for each item are derived from the results submitted by participants after eliminating the apparent blunders following Algorithm A in Annex C (normative) of ISO 13528.

The samples are from CRM (certified reference material) and a reference value from provider is to be compared with the assigned value. The standard deviation for proficiency assessment is set with reference to data obtained from a round of proficiency testing scheme.

Interpretation of the report

For the evaluation of performance, the interpretation is as follow:

$|z| \leq 2.0$ Satisfactory, $2.0 < |z| < 3.0$ Questionable, $|z| \geq 3.0$ Unsatisfactory

8. Confidentiality

To preserve this confidentiality, participants receive reports giving all results for that assessment but without identifying individual laboratories. The code number (M-***) assigned to a participant in this program is made known to the contact person or authorized person of his laboratory and the respective nominating accreditation body when the application is accepted.

9. General Information

For general queries, please contact us:

Yun S. Kim Ph.D. (Water Quality Research Center, K-water)
Tel.: +82-42-629-2041
Fax: +82-42-629-2099
E-mail: yunskim@kwater.or.kr, awesome40@kwater.or.kr
Address: Water Quality Research Center, K-water
200 Sinsangjinro, Daedeok, Daejeon, 34350, Korea

APLAC Proficiency Testing Programme (APLAC T104)
Trace Elements in Drinking Water

RECEIPT FORM

(Trace Elements in Drinking Water)

In order to monitor the progress of inter-laboratory comparisons, we kindly ask each laboratory to fill in this "***RECEIPT FORM***" and fax or e-mail the form to the contact information provided afterwards.

Thank you in advance for your cooperation.

The sample was received on: (date)

After inspection, were the contents damaged? (yes/no)

If yes, were the contents seriously damaged? (yes/no)

If yes, were the contents still suitable for use? (yes/no)

Remarks: _____

Participating Laboratory:

Contact Person:

Fax:

E-mail:

Water Quality Research Center, K-water
Yun S. Kim
Tel.: +82-42-629-2041, **Fax:** +82-42-629-2099
E-mail: yunskim@kwater.or.kr, awesome40@kwater.or.kr
Address: Water Quality Research Center, K-water
200 Sihimjiro, Daedeok, Daejeon, Republic of Korea 34350

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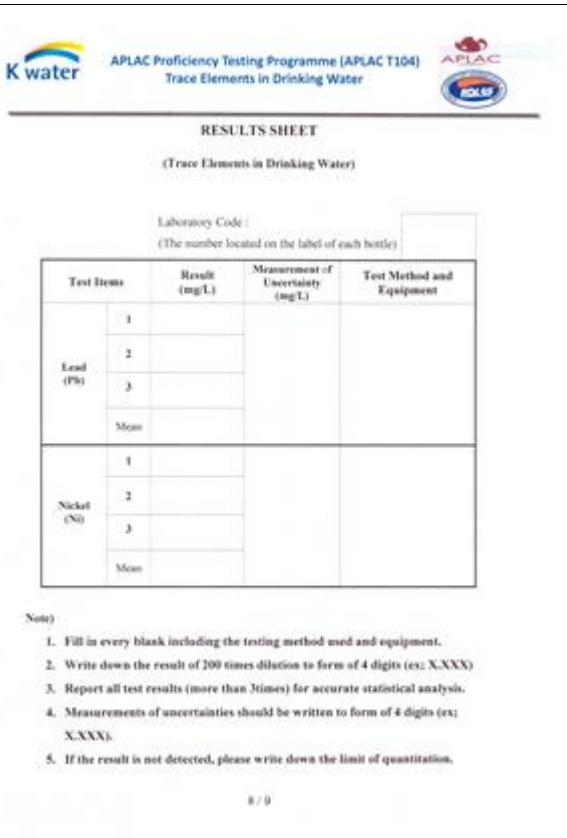

APLAC Proficiency Testing Programme (APLAC T104)
Trace Elements in Drinking Water

RESULTS SHEET

(Trace Elements in Drinking Water)

Laboratory Code :
(The number located on the label of each bottle)

Test Items		Result (mg/L)	Measurement of Uncertainty (mg/L)	Test Method and Equipment
Lead (Pb)	1			
	2			
	3			
	Mean			
Nickel (Ni)	1			
	2			
	3			
	Mean			

Note)

1. **Fill in every blank including the testing method used and equipment.**
2. **Write down the result of 200 times dilution to form of 4 digits (ex: X.XXX)**
3. **Report all test results (more than 3times) for accurate statistical analysis.**
4. **Measurements of uncertainties should be written to form of 4 digits (ex: X.XXX).**
5. **If the result is not detected, please write down the limit of quantitation.**

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APLAC Proficiency Testing Programme (APLAC T104)
Trace Elements in Drinking Water

Remarks: _____

(Comment your opinion on this PT program)

Participating Laboratory:

Contact Person:

Fax:

E-mail:

Date:

Signature:

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