Performance Report for Proficiency Testing

KOLAS PT-2012-09, Metals (Lead and Copper) in Water

KOLAS PROFICIENCY TESTING PROGRAM

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KOLAS (Korea Laboratory Accreditation Scheme)

SUMMARY

1. Proficiency Testing 『PT-2012-09, Metals (Lead and Copper) in Water』 is designed for laboratories that are accredited or wish to join the test. The samples for the test were initially distributed on June 11, 2012, and the deadline for submitting the testing results was July 7, 2012. There were 83 participants for Lead and 85 participants for Copper.

2. Artifacts (test samples) were prepared by K-water with testing homogeneity and stability based on ISO Guide 35. One artifact (20 mL) was provided to the participants and they were to complete the test after 100 times dilution and write down their results without any conversions.

3. Performance of the participating laboratories was assessed using Robust statistics based on ISO 13528. The assigned value for each item was derived from the consensus of the results submitted by participants, and the standard deviation for proficiency was set with reference to data obtained from a round of proficiency testing scheme.

4. The results of proficiency testing for participants using z-score are given in the following table.

Items	Assigned Value (mg/L)	Satisfactory	Questionable	Unsatisfactory	Number of participating laboratories
		$\lvert z \rvert \leq 2$	$2 < \lvert z \rvert < 3$	$3 \leq \lvert z \rvert$	
Lead	2.520	66	8	9	83
Copper	1.800	67	7	11	85

1. INTRODUCTION

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

K-water's Water Analysis and Research Center is the proficiency testing provider accredited by KOLAS (Korea Laboratory Accreditation Scheme) for the design, preparation, and operation of PT schemes that meet the requirements of ISO/IEC 17043. K-water operated PT-2012-09, Metals (Lead and Copper) in Water for laboratories which wanted to participate.

The operating period was from June 11, 2012 to July 7, 2012 and the total number of participating laboratories was 86 for Lead and Copper, 83 for Lead, 85 for Copper. There were 8 non-accredited participants for each item.

Table 1. Participants

Items	Lead	Copper
Participating laboratories (ISO/IEC 17025 Accredited laboratories)	83 (75)	85 (77)

This report is the final report for describing the introduction and determination of assigned values, reporting of data, and evaluation of participants.

2. DESIGN AND OPERATION OF PT PROGRAM

2.1 Preparation of Artifacts

The artifacts (testing samples) were prepared by K-water, and distributed after testing availability for homogeneity and stability. And the concentration of the sample was decided considering usual analysis concentrations and abilities of testing equipment.

Table 2. Concentration range for artifacts

Lead	Copper
(0.5 ~ 20.0) mg Pb/L	(0.5 ~ 20.0) mg Cu/L

2.2 Distribution of Artifacts

One artifact (20 mL each) was provided to the participants, with each one having been labeled Laboratory Code (M1 ~ M208) to ensure confidentiality of the results. The participants sent the results of the 100 times dilution.

Table 3. Distribution of artifacts

Random Selection (M1 ~ M208)	Packaged and sent by Air freight
	

3. PERFORMANCE ASSESSMENT

3.1 Results of participants

Table 4 shows the results and MU (Measurement of Uncertainty) of 86 participants.

Table 4. Results and MU (N/S : Not submitted)

No.	Lab. Code	Lead		Copper	
		Result (mg/L)	MU (mg/L)	Result (mg/L)	MU (mg/L)
1	M-1	2.31	0.01	1.66	0.01
2	M-2	2.67	0.30	2.15	0.20
3	M-3	2.60	0.40	1.8	0.10
4	M-5	2.52	0.15	1.86	0.06
5	M-6	2.84	0.66	1.86	0.22
6	M-7	2.53	0.10	1.92	0.10
7	M-10	2.52	0.10	1.87	0.10
8	M-11	2.60	0.10	1.8	0.10
9	M-12	2.51	0.10	1.83	0.10
10	M-15	2.52	0.10	1.77	0.10
11	M-16	2.52	0.20	1.89	0.20
12	M-19	2.41	0.03	1.76	0.01
13	M-20	2.54	0.11	1.84	0.12
14	M-21	2.48	0.06	1.76	0.06
15	M-23	2.60	0.20	1.80	0.10
16	M-24	2.50	0.10	1.80	0.10
17	M-28	2.50	0.10	1.80	0.10
18	M-29	2.44	N/S	1.75	N/S
19	M-40	2.50	N/S	1.70	N/S
20	M-42	2.74	0.66	1.81	0.22
21	M-46	2.58	0.41	1.84	0.22
22	M-47	2.45	0.09	1.77	0.08
23	M-48	2.46	0.10	1.74	0.07
24	M-49	2.40	0.05	1.87	0.07
25	M-50	2.52	0.00	1.82	0.00
26	M-56	1.90	N/S	2.50	N/S

** The results are rounded off to three decimal places, MU are raised to a unit.*

Table 4. Results and MU (Continued) (N/S : Not submitted)

No.	Lab. Code	Lead		Copper	
		Result (mg/L)	MU (mg/L)	Result (mg/L)	MU (mg/L)
27	M-57	2.51	0.04	1.81	0.02
28	M-59	2.53	0.10	1.77	0.10
29	M-60	2.60	0.30	1.80	0.20
30	M-69	2.30	0.17	1.68	0.12
31	M-71	2.60	0.40	1.80	0.30
32	M-72	2.59	0.19	1.86	0.18
33	M-73	2.50	0.50	1.80	0.08
34	M-75	2.50	4.50	1.70	5.00
35	M-79	-	-	187.19	1.20
36	M-81	2.73	N/S	1.91	N/S
37	M-82	2.58	0.03	1.79	0.04
38	M-84	2.40	0.17	1.52	0.11
39	M-85	2.58	0.03	1.72	0.01
40	M-88	2.66	0.02	1.75	0.02
41	M-91	2.54	N/S	1.83	N/S
42	M-92	2.81	N/S	2.04	N/S
43	M-95	2.46	0.50	1.79	0.50
44	M-99	2.69	0.02	1.87	0.01
45	M-103	2.21	0.02	1.65	0.015
46	M-104	2.50	0.10	1.80	0.10
47	M-106	253.40	11.40	180.60	6.10
48	M-107	0.62	0.05	-	-
49	M-108	2.58	0.01	1.82	0.05
50	M-110	2.52	6.40	1.87	8.40
51	M-112	2.60	N/S	1.80	N/S
52	M-117	-	-	1.80	0.05
53	M-119	2.52	0.08	1.75	0.07
54	M-120	2.44	0.01	1.76	0.01
55	M-123	2.72	0.14	1.93	0.12
56	M-125	2.46	0.03	1.79	0.02

** The results are rounded off to three decimal places, MU are raised to a unit.*

Table 4. Results and MU (Continued) (N/S : Not submitted)

No.	Lab. Code	Lead		Copper	
		Result (mg/L)	MU (mg/L)	Result (mg/L)	MU (mg/L)
57	M-126	2.67	0.07	1.87	0.05
58	M-127	2.52	0.05	1.79	0.05
59	M-128	2.59	0.13	1.79	0.16
60	M-129	2.38	0.38	1.71	0.26
61	M-133	2.49	0.03	1.71	0.03
62	M-139	2.32	0.06	1.72	0.05
63	M-143	2.58	0.21	1.91	0.21
64	M-153	2.51	0.00	1.80	0.00
65	M-159	2.54	0.10	1.80	0.30
66	M-160	2.50	0.20	1.70	0.10
67	M-161	2.54	0.21	1.93	0.39
68	M-162	2.61	0.13	1.83	0.07
69	M-163	2.52	0.15	1.82	0.11
70	M-164	2.50	0.06	1.80	0.06
71	M-165	2.50	0.08	1.80	0.06
72	M-168	2.88	0.07	2.08	0.05
73	M-169	2.51	0.03	1.80	0.02
74	M-171	2.31	0.10	1.80	0.10
75	M-173	2.37	0.08	1.79	0.06
76	M-174	2.50	0.08	1.80	0.06
77	M-187	2.61	0.19	1.92	0.19
78	M-190	-	-	177.20	3.00
79	M-191	2.81	0.18	2.94	0.23
80	M-192	2.46	0.14	1.78	0.06
81	M-193	266	19.15	200.90	19.26
82	M-194	2.50	0.03	1.83	0.03
83	M-196	2.50	0.20	1.80	0.20
84	M-197	2.60	0.48	1.82	0.34
85	M-201	2.48	0.30	1.86	0.10
86	M-208	2.29	0.04	1.59	0.03

** The results are rounded off to three decimal places, MU are raised to a unit.*

3.2 Performance assessment

Performance of the participating laboratories will be assessed using *z*-score* which is detailed in Table 5. The assigned value for each item was derived from either the consensus of the results submitted by participants, and the standard deviation for proficiency was set with reference to data obtained from a round of proficiency testing scheme. More detailed calculations are shown in Annex C (normative) Robust analysis from ISO 13528.

Table 5. Determination of the assigned value and the standard deviation from ISO 13528

Determination	Method
5.1 Choice of method for determining the assigned value ($\hat{x}$)	5.2 Formulation 5.3 Certified reference values 5.4 Reference value 5.5 Consensus values from expert laboratories **5.6 Consensus value from participants** 5.7 Comparison of the assigned value 5.8 Missing values
6.1 Choice of method for determining the standard deviation ($\hat{\sigma}$)	6.2 Prescribed value 6.3 By perception 6.4 From a general model 6.5 From the results of a precision experiment **6.6 From data obtained from a round of a proficiency testing scheme** 6.7 Comparison of precision values derived from a proficiency test with established values

ISO 13528 4.2 (Guidelines for limiting the uncertainty of the assigned value) says that if the measurement of uncertainty is less than standard deviation times 0.3 ($u_x \leq 0.3\,\hat{\sigma}$), the measurement of uncertainty can be ignored and does not have to be included in the interpretation of results.

The calculated results of assigned values and standard deviations for this proficiency test are given in Table 6.

Table 6. Calculation of assigned value and Standard deviation

Classification	Lead	Copper
Assigned value ($\hat{x}$, mg/L)	2.520	1.800
MU for the assigned value* (u_x, mg/L)	0.013 1	0.008 9
Standard deviation ($\hat{\sigma}$, mg/L)	0.089 0	0.059 3
0.3 × Standard deviation ($\hat{\sigma}$)	0.026 7	0.017 8

** MU for the assigned value*: measurement of uncertainty for deciding assigned value when 'Consensus value from participants' method is used*

Both items' measurement of uncertainty is less than standard deviation times 0.3. The z-score was used for performance of the participating laboratories.

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

x : reported result of an individual participant
$\hat{x}$: assigned value
$\hat{\sigma}$: standard deviation of participants' results

z-score is commonly interpreted as:

$|z| \leq 2$ Satisfactory
$2 < |z| < 3$ Questionable
$3 \leq |z|$ Unsatisfactory

(*) For more detailed information, please refer to ' ISO 13528'.

4. PERFORMANCE EVALUATION

4.1 Results for participants

Results for participants using z-score are given in Tables 7 ~ 10. There were some questionable and unsatisfactory participants; 17 for Lead and 18 for Copper.

There were 8 questionable and 9 unsatisfactory participants out of a total of 83 participants for the Lead item, and the distribution of z-score is given in Figure 1.

Table 7. Results for Lead

Items	Satisfactory	Questionable	Unsatisfactory	Number of participating laboratories
	$\lvert z \rvert \leq 2$	$2 < \lvert z \rvert < 3$	$3 \leq \lvert z \rvert$	
Lead	66	8	9	83

** Questionable (8): M-1, M-42, M-69, M-81, M-123, M-139, M-171, M-208*

** Unsatisfactory (9): M-6, M-56, M-92, M-103, M-106, M-107, M-168, M-191, M-193*

There were 7 questionable and 11 unsatisfactory participants out of a total of 85 participants for the Copper item, and the distribution of z-score is given in Figure 2.

Table 8. Results for Copper

Items	Satisfactory	Questionable	Unsatisfactory	Number of participating laboratories
	$\lvert z \rvert \leq 2$	$2 < \lvert z \rvert < 3$	$3 \leq \lvert z \rvert$	
Copper	67	7	11	85

** Questionable (7): M-1, M-7, M-69, M-103, M-123, M-161, M-187*

** Unsatisfactory (11): M-2, M-56, M-79, M-84, M-92, M-106, M-168, M-190, M-191, M-193, M-208*

Table 9. Results and z-score for Lead (Result : mg/L)

No.	Lab. Code	Result	*z*-score	No.	Lab. Code	Result	*z*-score
1	**M-1**	**2.31**	**-2.36**	43	M-99	2.69	1.91
2	M-2	2.67	1.69	44	**M-103**	**2.21**	**-3.48**
3	M-3	2.60	0.90	45	M-104	2.50	-0.22
4	M-5	2.52	0.00	46	**M-106**	**253.40**	**2819.51**
5	**M-6**	**2.84**	**3.60**	47	**M-107**	**0.62**	**-21.35**
6	M-7	2.53	0.11	48	M-108	2.58	0.67
7	M-10	2.52	0.00	49	M-110	2.52	0.00
8	M-11	2.60	0.90	50	M-112	2.60	0.90
9	M-12	2.51	-0.11	51	M-119	2.52	0.00
10	M-15	2.52	0.00	52	M-120	2.44	-0.90
11	M-16	2.52	0.00	53	**M-123**	**2.72**	**2.25**
12	M-19	2.41	-1.24	54	M-125	2.46	-0.67
13	M-20	2.54	0.22	55	M-126	2.67	1.69
14	M-21	2.48	-0.45	56	M-127	2.52	0.00
15	M-23	2.60	0.90	57	M-128	2.59	0.79
16	M-24	2.50	-0.22	58	M-129	2.38	-1.57
17	M-28	2.50	-0.22	59	M-133	2.49	-0.34
18	M-29	2.44	-0.90	60	**M-139**	**2.32**	**-2.25**
19	M-40	2.50	-0.22	61	M-143	2.58	0.67
20	**M-42**	**2.74**	**2.47**	62	M-153	2.51	-0.11
21	M-46	2.58	0.67	63	M-159	2.54	0.22
22	M-47	2.45	-0.79	64	M-160	2.50	-0.22
23	M-48	2.46	-0.67	65	M-161	2.54	0.22
24	M-49	2.40	-1.35	66	M-162	2.61	1.01
25	M-50	2.52	0.00	67	M-163	2.52	0.00
26	**M-56**	**1.90**	**-6.97**	68	M-164	2.50	-0.22
27	M-57	2.51	-0.11	69	M-165	2.50	-0.22
28	M-59	2.53	0.11	70	**M-168**	**2.88**	**4.05**
29	M-60	2.60	0.90	71	M-169	2.51	-0.11
30	**M-69**	**2.30**	**-2.47**	72	**M-171**	**2.31**	**-2.36**
31	M-71	2.60	0.90	73	M-173	2.37	-1.69
32	M-72	2.59	0.79	74	M-174	2.50	-0.22
33	M-73	2.50	-0.22	75	M-187	2.61	1.01
34	M-75	2.50	-0.22	76	**M-191**	**2.81**	**3.26**
35	**M-81**	**2.73**	**2.36**	77	M-192	2.46	-0.67
36	M-82	2.58	0.67	78	**M-193**	**266.00**	**2961.11**
37	M-84	2.40	-1.35	79	M-194	2.50	-0.22
38	M-85	2.58	0.67	80	M-196	2.50	-0.22
39	M-88	2.66	1.57	81	M-197	2.60	0.90
40	M-91	2.54	0.22	82	M-201	2.48	-0.45
41	**M-92**	**2.81**	**3.26**	83	**M-208**	**2.29**	**-2.58**
42	M-95	2.46	-0.67	* *Statistical treatment after rounding off the result.*			

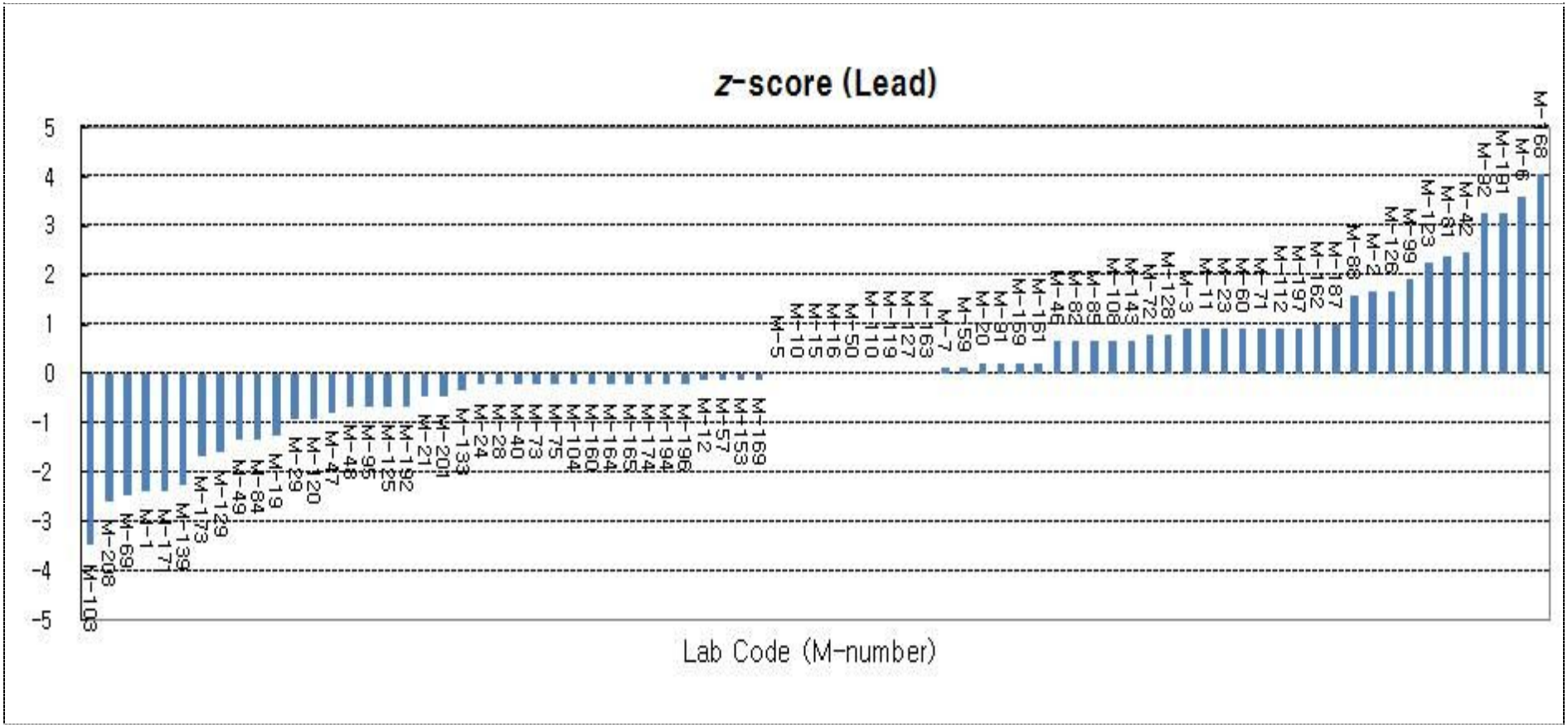

Figure 1. z-score distribution for Lead

** Significant outliers are excluded in the picture (4); M-56, M-106, M-107, M-193*

** Unsatisfactory (9): M-6, M-56, M-92, M-103, M-106, M-107, M-168, M-191, M-193*

** Questionable (8): M-1, M-42, M-69, M-81, M-123, M-139, M-171, M-208*

Table 10. Results and z-score for Copper (Result : mg/L)

No.	Lab. Code	Result	*z*-score	No.	Lab. Code	Result	*z*-score
1	**M-1**	**1.66**	**-2.36**	44	M-99	1.87	1.18
2	**M-2**	**2.15**	**5.90**	45	**M-103**	**1.65**	**-2.53**
3	M-3	1.80	0.00	46	M-104	1.80	0.00
4	M-5	1.86	1.01	47	**M-106**	**180.60**	**3014.16**
5	M-6	1.86	1.01	48	M-108	1.82	0.34
6	**M-7**	**1.92**	**2.02**	49	M-110	1.87	1.18
7	M-10	1.87	1.18	50	M-112	1.80	0.00
8	M-11	1.80	0.00	51	M-117	1.80	0.00
9	M-12	1.83	0.51	52	M-119	1.75	-0.84
10	M-15	1.77	-0.51	53	M-120	1.76	-0.67
11	M-16	1.89	1.52	54	**M-123**	**1.93**	**2.19**
12	M-19	1.76	-0.67	55	M-125	1.79	-0.17
13	M-20	1.84	0.67	56	M-126	1.87	1.18
14	M-21	1.76	-0.67	57	M-127	1.79	-0.17
15	M-23	1.80	0.00	58	M-128	1.79	-0.17
16	M-24	1.80	0.00	59	M-129	1.71	-1.52
17	M-28	1.80	0.00	60	M-133	1.71	-1.52
18	M-29	1.75	-0.84	61	M-139	1.72	-1.35
19	M-40	1.70	-1.69	62	M-143	1.91	1.85
20	M-42	1.81	0.17	63	M-153	1.80	0.00
21	M-46	1.84	0.67	64	M-159	1.80	0.00
22	M-47	1.77	-0.51	65	M-160	1.70	-1.69
23	M-48	1.74	-1.01	66	**M-161**	**1.93**	**2.19**
24	M-49	1.87	1.18	67	M-162	1.83	0.51
25	M-50	1.82	0.34	68	M-163	1.82	0.34
26	**M-56**	**2.50**	**11.80**	69	M-164	1.80	0.00
27	M-57	1.81	0.17	70	M-165	1.80	0.00
28	M-59	1.77	-0.51	71	**M-168**	**2.08**	**4.72**
29	M-60	1.80	0.00	72	M-169	1.80	0.00
30	**M-69**	**1.68**	**-2.02**	73	M-171	1.80	0.00
31	M-71	1.80	0.00	74	M-173	1.79	-0.17
32	M-72	1.86	1.01	75	M-174	1.80	0.00
33	M-73	1.80	0.00	76	**M-187**	**1.92**	**2.02**
34	M-75	1.70	-1.69	77	**M-190**	**177.20**	**2956.84**
35	**M-79**	**187.19**	**3125.25**	78	**M-191**	**2.94**	**19.22**
36	M-81	1.91	1.85	79	M-192	1.78	-0.34
37	M-82	1.79	-0.17	80	**M-193**	**200.90**	**3356.37**
38	**M-84**	**1.52**	**-4.72**	81	M-194	1.83	0.51
39	M-85	1.72	-1.35	82	M-196	1.80	0.00
40	M-88	1.75	-0.84	83	M-197	1.82	0.34
41	M-91	1.83	0.51	84	M-201	1.86	1.01
42	**M-92**	**2.04**	**4.05**	85	**M-208**	**1.59**	**-3.54**
43	M-95	1.79	-0.17				

** Statistical treatment after rounding off the result.*

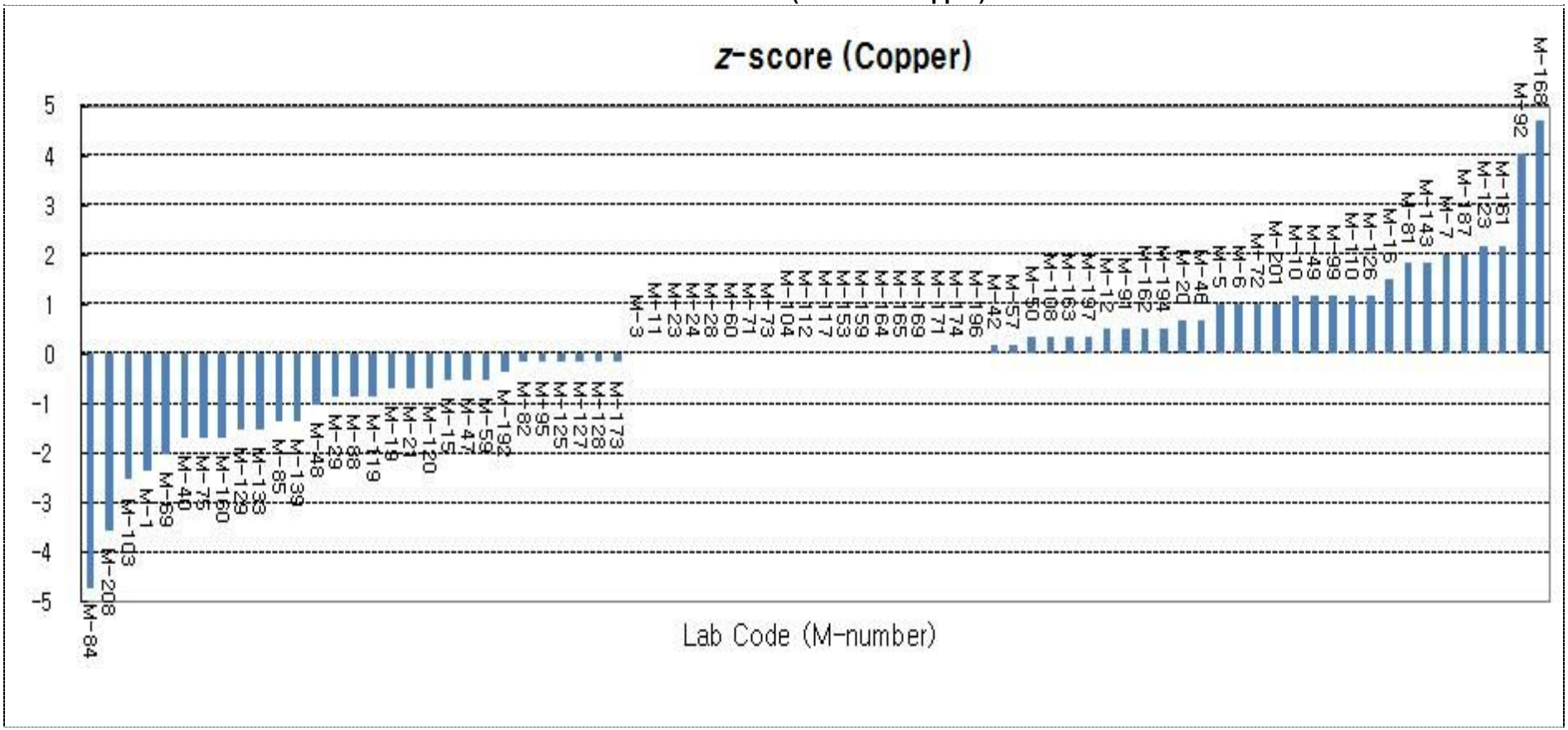

Figure 2. z-score distribution for Copper

** Significant outliers are excluded in the picture (7); M-2, M-56, M-79, M-106, M-190, M-191, M-193*

** Unsatisfactory (11): M-2, M-56, M-79, M-84, M-92, M-106, M-168, M-190, M-191, M-193, M-208*

** Questionable (7): M-1, M-7, M-69, M-103, M-123, M-161, M-187*

4.2 Results and MU (measurement of uncertainty)

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

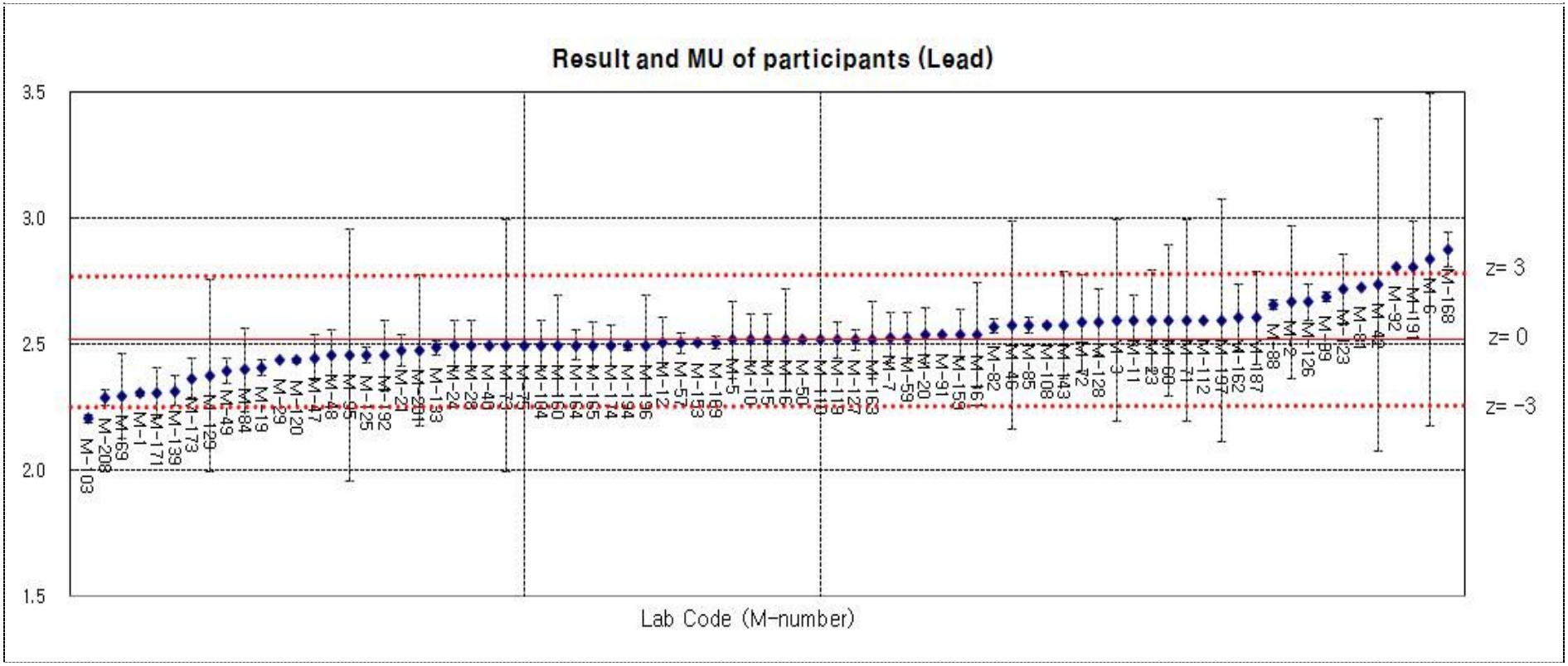

Figure 3. Results and MU of participants for Lead

** MU: Measurement of uncertainty*

** Significant outliers are excluded in the picture; M-56, M-106, M-107, M-193*

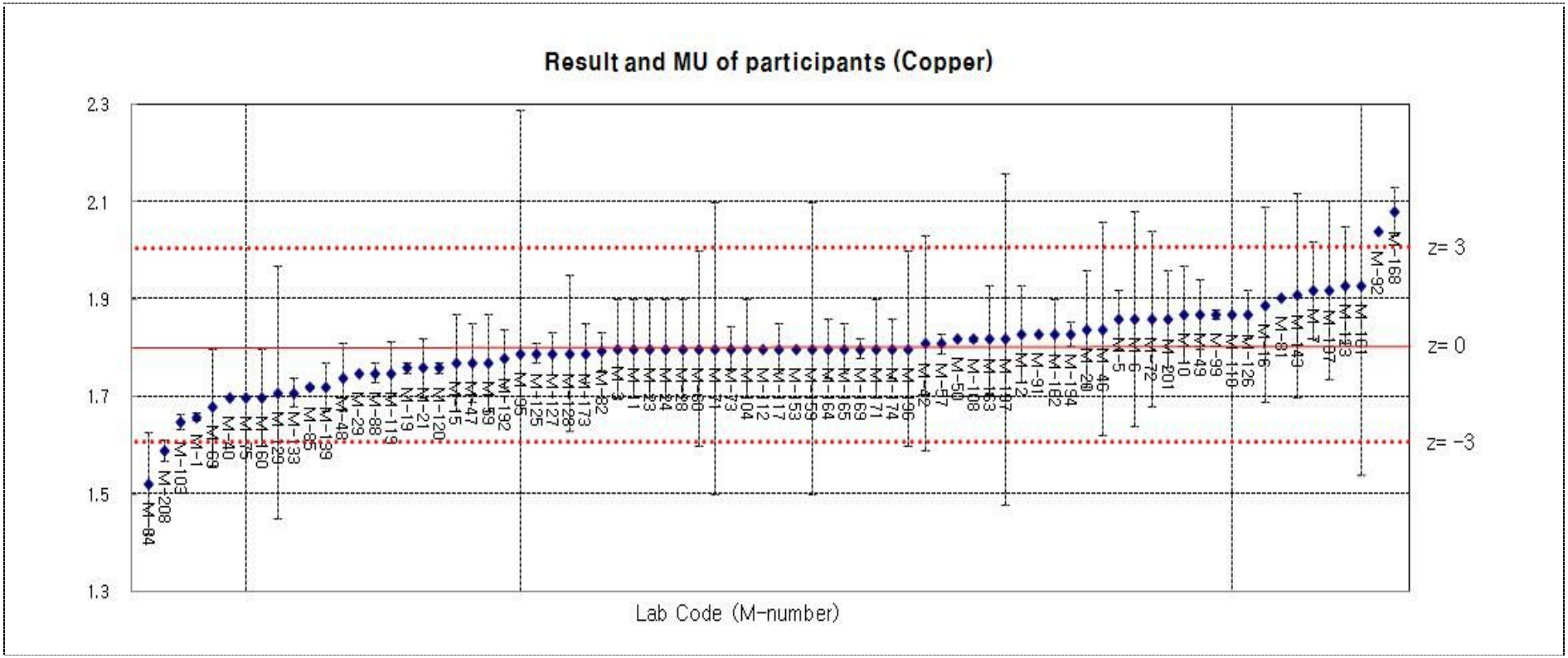

Figure 3. Results and MU of participants for Copper

** MU: Measurement of uncertainty*

** Significant outliers are excluded in the picture; M-2, M-56, M-79, M-106, M-190, M-191, M-193*

Laboratories not submitting MU or having too large or small MU compared to the results are recommended to self-evaluate affecting factors.

4.3 Test method and equipment

Most laboratories are using their national test methods as a routine method. The methods are classified into 4 majors; 1) Spectrophotometry, 2) AAS (Atomic Absorption Spectrophotometry), 3) ICP-AES, -OES (Inductively Coupled Plasma -Atomic Emission Spectrometry, -Optical Emission Spectrometry), 4) ICP-MS (Inductively Coupled Plasma Mass Spectrometry). A comparison of the test methods are shown in table 11.

When the methods are compared with the results, their effects are insignificant.

Table 11. Comparison of test methods

Test method	Number of participants	Laboratory code
Total	86	
Spectro-photometry	2	M-85, M-117
AAS	11	M-10, M-12, M-19, M-20, M-23, M-56, M-69, M-79, M-81, M-107, M-201
ICP-AES, ICP-OES	56	M-3, M-5, M-6, M-11, M-15, M-16, M-21, M-24, M-29, M-40, M-42, M-46, M-47, M-48, M-50, M-57, M-60, M-71, M-75, M-82, M-84, M-88, M-91, M-92, M-95, M-99, M-103, M-104, M-106, M-119, M-120, M-123, M-125, M-126, M-127, M-133, M-139, M-143, M-153, M-159, M-160, M-161, M-162, M-163, M-164, M-165, M-168, M-169, M-174, M-187, M-190, M-192, M-193, M-194, M-196, M-197
ICP-MS	17	M-1, M-2, M-7, M-28, M-49, M-59, M-72, M-73, M-108, M-110, M-112*, M-128, M-129, M-171, M-173, M-191, M-208

** M-112*: used all methods (ICP-AES, -OES and ICP-MS), classified and written in ICP-MS for middle point.*

5. CONCLUSION

Laboratories having unsatisfactory or questionable statistical evaluations shall have to be thoroughly investigated to determine the discrepancy for the management system, technical requirements such as reference materials, glasses, calibrations for test equipment, and test methods. Also, they shall have to consider personnel training, prevention and correction for test enhancement.

Laboratories having satisfactory statistical evaluations but a broad range for the measurement of uncertainty are recommended to review reference materials, glasses, calibrations for test equipment, and test methods.